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The Conductance of Some Non-Rigid Bolaform Electrolytes

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THE CONDUCTANCE OF SOME NON-RIGID BOLAFORM ELECTROLYTES

(TITLE)

BY

William Terry Schmidt

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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CHARLESTON, ILLINOIS

1972
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ABSTRACT

Title of Thesis: The Conductance of Some Non-Rigid Bolaform Electrolytes

William Terry Schmidt, Master of Science , 1972

Thesis directed by : David W. Ebdon, Assistant Professor of Chemistry

Bolaform electrolytes are those which contain two or more charges separated by an inert framework. These are intermediate in structure between simple electrolytes and polyelectrolytes. Since these are similar to both synthetic and biological electrolytes, this investigation has been undertaken to determine some of their properties in solution.

The sodium and magnesium salts of ethane, propane, butane, pentane, hexane and decane α,ω-disulfonates were prepared. Each acid was prepared by refluxing the α,ω-dibromide of the desired salt with sodium sulfite. The sodium and magnesium salts were prepared by ion-exchange techniques.

The conductance of each salt was determined in methanol utilizing the weight dilution method. A data treatment method for unsymmetrical 1-2 electrolytes was tested. The Murphy-Cohen equation:

$$\Lambda = \Lambda^{\circ} - S\sqrt{C} + E'C\ln C + J'C$$

was found to be invalid in the concentration range studied, 1.0 - 5.0 x 10^{-4}moles/liter. The Onsager limiting law when applied to the sodium salt data gave Λ° values from approximately 108 ($ohm^{-1}cm^2equiv^{-1}$) for the ethane salt to 100 ($ohm^{-1}cm^2equiv^{-1}$) for the decane. Phoreograms showed these salts to be unassociated in methanol. The magnesium salts

deviated substantially below the limiting law plot and consequently were considered highly associated.

The Λ° values for the magnesium salts were calculated from Kohlrausch's law, $\Lambda^\circ = \lambda^+_{Mg} + \lambda^-_{anion}$. By fixing this value, association constants were found to be in a range of 108,950 for the ethane salt to 25,260 for the decane salt. These values show a monotonic decrease as the chain length of the salt increases. This is explained by charge separation considerations. As the chain length increases the charge density on the molecule decreases, illustrating a decrease in ion-ion interactions.

The frictional coefficients of the sodium salts were determined from λ^- data. These showed values of .0496 X 10^{-7} g/sec for the ethane salt to .0563 X 10^{-7} g/sec for decane salts. The Peterlin rod and bead model for the determination of frictional forces was successfully applied to the data.

The Perrin rigid ellipsoid model did not show any agreement when experimental and theoretical frictional coefficient values were compared.

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GLOSSARY OF SYMBOLS

a	hydrodynamic radius of the i th ion
b	interbead separation
C	concentration in moles per liter in the conductance cell
D	dielectric constant
e	electronic charge, 4.8×10^{-10} esu
λ_i	equivalent conductance of the i th ion
λ_i^o	equivalent ionic conductance at infinite dilution
Z	ionic charge
z	degree of polymerization, number of beads
η_o	solvent viscosity, in poise
a'	semi-minor axis of ellipsoid
b'	semi-major axis of ellipsoid
Λ	equivalent conductance, $ohm^{-1}cm^2equiv^{-1}$
Λ_o	equivalent conductance at infinite dilution
$\bar{C}$	concentration of stock solution moles solute/gm stock
N	equivalent concentration equiv/l
L	specific conductance ohm^{-1}
L_m	measured specific conductance
L_s	specific conductance of solute
R_∞	resistance extrapolated to infinite frequency
V	volume, liters
S	conductance equation constant dependent on D, η, T and Λ_o

E'	conductance equation constant dependent on D, η, T and Λ_o
J'	conductance equation constant dependent on a_j, D, η, T and Λ_o
Λ'	function for conductance data treatment
α	degree of dissociation
K_A	association constant
ν	number of ions produced by a species
k	Boltzmann constant
T	absolute temperature, °K
ζ	frictional coefficient of anion
ζ_o	frictional coefficient on single bead
ω_i	ionic mobility of the i th ion
θ	valence angle between beads

INTRODUCTION

In developing the theories and equations concerning conductivity, one must first describe the behavior of ions in solution. The ion is approximated as a hard sphere surrounded by a homogeneous medium of solvent molecules having continous dielectric constant. This is no longer a valid assumption when the average distance between the ions is small. The reason for this breakdown is that the dielectric constant in this region is no longer described by the macroscopic dielectric constant of the solvent. Therefore, ionic size, structure, charge, even dipole moments will affect the extent of interaction.

The ion-ion interactions are clearly concentration dependent and may be thought of, in part, as frictional effects on the ions as they travel through the solutions. These effects are responsible for any deviations from theoretical behavior in solution.

Ion-solvent interactions are also an important consideration. Ion-ion and ion-solvent interactions are competitive and dependent upon one another.

Studies have shown that the alkali metal and alkaline earth salts of p-benzenedisulfonic acids are unassociated in water[1]. The large negative charge of the disulfonate group and its interaction with nearby water molecules give graphic results of ion-solvent interactions overriding ion-ion interactions. This reduces the tendency toward association.

Additional studies on a series of aryl polysulfonates of regularly increasing size have shown some association to occur as the

dielectric constant of the solvent decreases[2]. This is due to the decrease in ion-solvent interactions and formation of ion pairs.

The Onsager limiting law, $\Lambda = \Lambda^\circ - S\sqrt{C}$[3], embodies corrections for both ion-ion and ion-solvent effects in the constant S. The Fuoss-Onsager equation improves the limiting law by the addition of two terms EClogC and JC.[4] This improvement is based upon the assumption that the electrolyte is completely dissociated in solution.

For electrolytes which are associated and unsymmetrical the Fuoss-Edelson technique[5] has been used with some success[6]. This technique employs only the Onsager limiting law and is thus limited to very dilute solutions.

An equation by Murphy and Cohen[7] has been derived which improves the E and J terms of the Fuoss-Onsager equation. This equation is purported to be applicable to both symmetrical and unsymmetrical electrolytes.

Theories of conductivity should be capable of: [a] predicting Λ° from the dimensions, charges and other properties of the ions and the solvent molecules, [b] predicting the value of the constant S in the limiting law, and [c] accounting quantitatively for deviations from the limiting law at higher concentrations[8]. Capabilities [b] and [c] are well accounted for in the preceding discussion; however, methods of prediction of values for Λ° are not well known.

An attempt to correlate models of bolaform electrolytes to obtain transport properties has been made by Rice[9,10]. Bolaform electrolytes are molecules containing two or more charges separated by an inert framework. An abbreviated theoretical treatment follows.

The ionic mobility is

$$\omega_i = \frac{300\ \lambda_i}{96{,}494|Z_i|e} \quad \text{[ionic mobility of the } \underline{i} \text{ th ion]},$$

where λ_i = equivalent conductance of the $\underline{i}$ th ion,

$|Z_i|$ = absolute charge on the $\underline{i}$ th ion, and

e = electronic charge [in esu].

From Stokes' law

$$\frac{1}{\omega_i} = \zeta = 6\Pi\eta_o a_i,$$

ζ = frictional coefficient,

η_o = solvent viscosity, and

a_i = hydrodynamic radius of the $\underline{i}$ th ion.

There have been two predominate models proposed for the determination of the frictional forces exerted upon a molecule as it travels through the solvent. They are the rod and bead model and the rigid ellipsoid model.

For the rod and bead model, two assumptions must be made: [a] the hydrodynamic situation can best be described by the usual equations of viscous fluid motion with all effects due to the molecular nature of the flow process absorbed into a frictional coefficient for the chain subunit, [b] the molecule may be adequately approximated by a model in which a series of beads are connected by massless rods. There is a bead at the junction of every two rods, and the rods make a fixed angle $\Pi - \theta$ with one another. Based on this model Peterlin[11,12,13] has derived the following expression for the frictional coefficient.

$$\zeta = \frac{z\zeta^\circ}{1 + \frac{a^\circ}{z}\sum_p \frac{z - p}{r_p}}$$

ζ = frictional coefficient for the entire molecule,

ζ_o = frictional coefficient for a single bead,

z = degree of polymerization [number of beads], and

a_o = hydrodynamic radius of single bead from Stokes equation,

$$\zeta_o = 6\pi a_o \eta_o .$$

Values for the ratio ζ/ζ_o [in the form of η/η_o] have been calculated by Peterlin from z = 1 to 100, for various values of the "valence angle", $\pi - \theta$, and for several ratios of the bead diameter to the interbead separation [a/b].

If the molecule is rod-like the equation by Riseman and Kirkwood[14] defines the frictional coefficient as:

$$\zeta = \frac{6\pi\eta_o b_o z}{\ln z - \left[1 - \frac{6\pi\eta_o b_o}{2\zeta_o}\right]},$$

where b_o is the interbead separation.

The rigid - ellipsoid model of Perrin[15] leads to the expression

$$\frac{6\pi\eta_o (b'^2 - a'^2)^{1/2}}{\ln[b'/a') + \sqrt{(b'/a')^2 - 1}]} \xrightarrow{b' >> a'} \frac{6\pi\eta_o b'}{\ln[2b'/a']}$$

b' = semimajor axis of ellipsoid,

a' = semiminor axis of ellipsoid, and

η_o = solvent viscosity.

Application of experimentally determined parameters, such as equivalent conductance and size measurements of models to the above equations, allows one to predict conductances of homologous series of electrolytes.

Atkinson applied the rigid ellipsoid model to the rigid bolaform ions of para-benzenedisulfonate, p-$BDS^=$, and biphenyldisulfonate, $BPDS^=$, using benzenesulfonate, BS^-, to fix the necessary

parameters, and found the model to be in reasonable agreement[16] with the experiment. Staples also found this to be true for the terphenyldisulfonate, $TPDS^{=}$,ion[17].

Rice, Thompson, and Nagasawa[18] have verified these results through diffusion coefficient measurements.

Rice has treated the data of Fuoss[19,20] using the Peterlin rod and bead model for a system of non-rigid polymethylene diquaternary ammonium salts. This gives quite good agreement with the theory as compared to the rigid ellipsoid model as might be expected.

The non-rigid system has the capability of coiling back upon itself whereas the rigid phenyl rings are fixed in configuration.

Fuoss postulates this coiling of the non-rigid system as an explanation for anomalies in the second dissociation constant of these 1-2 electrolytes. "...the chain is probably curled up under the attractive field of the anion, because an extended configuration would lead to an increase of k_2 with increasing chain length, corresponding to diminished attraction from the unpaired charge on the cation ... k_2 will increase with increasing chain length, but less rapidly than would be predicted on the basis of the extended configuration."[19]

STATEMENT OF THE PROBLEM

The primary objective of this investigation is to test the Peterlin Rod and Bead Model for the determination of hydrodynamic parameters. This will be done for a series of non-rigid bolaform electrolytes of sodium polymethylene α,ω-disulfonates. The conductance of the pentane salt will be used to establish the necessary parameters. From these the frictional coefficients will be calculated and compared to the experimental values.

An important factor which may determine the results is the applicability of the Murphy-Cohen equation to electrolytes of the unsymmetrical 1-2 type. This equation will be tested to determine its validity through the concentration ranges studied.

The λ_o^- of sodium salts of ethane, propane, butane, pentane, hexane and decane disulfonic acids will be determined in methanol.

The λ_o^- of the magnesium salts of the above compounds will also be investigated utilizing the Murphy-Cohen equation for symmetrical 2-2 electrolytes.

Association of both salts will be studied and K_A values determined if association is present. This again depends upon the validity of the Murphy-Cohen equation.

EXPERIMENTAL

Polymethylene disulfonic acids. The following commercially prepared α,ω-dibromo-alkanes were obtained from Eastman Organic Chemicals, Rochester, New York.

		item no.
1-2	dibromoethane	130
1-3	dibromopropane	261
1-4	dibromobutane	4283
1-5	dibromopentane	1437
1-6	dibromohexane	4882
1-10	dibromodecane	4877

Twenty-five [25] grams of the dibromide was allowed to reflux with two-hundred [200] ml. of a saturated sodium sulfite [Na_2SO_3] solution until the organic layer disappeared. This signifies completion of the reaction and may require up to seven days. The solution was then cooled to 5°C and any product removed.

The 1,10-disulfodecane solidified upon reaching room temperature. This was taken up in a minimal amount of water for further workup.

The sulfate and sulfite present in the solution were removed by precipitation as barium salts with a saturated solution of barium hydroxide. It was necessary to centrifuge small portions of solution after each addition of hydroxide in order to determine when the

equivalence point was reached. An excess of base should be avoided. The barium salts were removed by filtration through filter-aid [Celite].

Free bromide in the solution was precipitated with silver oxide as silver bromide. The oxide was freshly prepared by precipitation from silver nitrate solution with sodium hydroxide, and the precipitate washed free of excess base.

At this point the solution was passed through an ion exchange column containing Dowex 50W-X8 cation exchange resin. The acidic solution was collected and reduced in a rotary evaporator.

The free acid may be obtained in the crystalline form by cooling to 5°C.

Other methods of preparation may be found in the literature.[21;22,23]

Sodium α,ω-polymethylene disulfonates. The acids from the preceding steps were used in these preparations.

The sodium salt was formed by the addition of sodium carbonate [Na_2CO_3] or sodium hydroxide solution to the acid. The acid was neutralized to a pH of approximately six [6]. This was monitored by hydrion paper, not a pH meter, to reduce amounts of extraneous ions admitted.

The sodium salt was obtained after reduction of volume and cooling to 0°C. All salts were recrystallized from conductivity water two times.

Magnesium α,ω-polymethylene disulfonates. The acid forms were prepared from the sodium salts by passing them through the cation exchange columns.

Powdered magnesium carbonate [$MgCO_3$] was added to the acid solution to a pH of approximately 6. Some excess carbonate was

precipitated as the volume was reduced by heating. This appeared before the magnesium salts began to precipitate and was removed. The salts were recrystallized once from conductivity water.

Both the sodium and magnesium salts are exceedingly soluble in water; several grams may be contained in just a few milliliters.

The salts were dried overnight at 100-110°C, ground in a mortar and pestle, and dried several hours before each run. They were stored in brown glass bottles in a desicator over $CaCl_2$ during the time they were in use.

Analysis. Neutralization equivalent analyses were done on each sodium salt. The salt was converted to the acid by the exchange column and titrated using a standardized NaOH base. Potassium acid phthalate [KHP] and potassium chloride were used for the standardization. The KCl was converted to the acid and titrated.

Table I. Analyses of the Sodium Salts

Salt	meq. cation calcd.	% cation found KHP	KCl
$Na_2(SO_3)_2(CH_2)_2$	2.104	99.9	----
$Na_2(SO_3)_2(CH_2)_3$	2.124	99.6	99.2
$Na_2(SO_3)_2(CH_2)_4$	2.102	99.6	99.2
$Na_2(SO_3)_2(CH_2)_5$	2.054	100.4	101.3
$Na_2(SO_3)_2(CH_2)_6$	1.834	100.0	98.8
$Na_2(SO_3)_2(CH_2)_{10}$	2.108	100.2	----

Meta-toluidine derivatives[21] of the sodium salts were prepared to determine isomeric purity of the compounds. The melting points of the derivatives are presented in Table II.

Table II. Derivatives of the Acids.

Salt	m-Toluidine[21] salts mp°C.	M.P.°C(Found)
$(SO_3H)_2(CH_2)_2$	230	---
$(SO_3H)_2(CH_2)_3$	222	220
$(SO_3H)_2(CH_2)_4$	214	213
$(SO_3H)_2(CH_2)_5$	187	190
$(SO_3H)_2(CH_2)_6$	158	---
$(SO_3H)_2(CH_2)_{10}$	178	180

The magnesium salts were titrated with Karl Fischer Reagent and no water was found to be present.

Purification of Solvents

Water. The conductivity water which was used for the recrystallization of the sodium salts was prepared by passing deionized water through two polishing exchange columns and monitoring quality with a built in conductivity cell. This water was found to contain small amounts of impurity, apparently iron hydroxide, so was not used for any conductivity runs.

The remainder of the water was collected from an all glass Corning AG-1b water distillation apparatus.

Due to the addition of new wings and air conditioning facilities to the science building, the environment in the physical chemistry laboratory did not allow one to obtain reproducible or even linear cell constants in water. For this reason, it was decided to do this work in methanol, and do the salts in water after completion of the building.

Methanol. All of the methanol used was purified according to a method used by Fuoss[24]. Approximately 2.5 liters of 99.9% pure methanol was allowed to reflux overnight, over a charge of 25 grams of aluminum powder with 5 grams mercuric chloride. The methanol was then distilled into a two liter receiving-dispensing flask. The fraction from 64.5°C to 64.9°C was collected.

Methanol of purity .09-.25 micromhos was used for the sodium salts and solvent of .01-.05 micromhos obtained for the magnesium salts.

Conductance Measurements

Equipment. The resistance measurements were made with a Beckman RC-18A Conductivity Bridge. One refinement was added to the bridge. The tenths decade was replaced by a variable, 1-ohm, 50 watt, Model J, Series A, Ohmite resistor. This was then calibrated and marked against a General Radio, Type 1433-F, decade resistor. A Heathkit Model IN 21 decade condensor was used as an external source of capacitance when needed.

A Sargent Thermonitor Model ST thermostat controlled the temperature of a nonconducting oil bath in a 15 gallon aquarium. Cooling is achieved by a few turns of copper tubing through which water at 20°C is pumped by a Forma Scientific Model 2095 Refrigerated and Heated Bath and Circulator. This achieves temperature control at 25.000±0.002°C.

Two Sargent magnetic stirrers were modified and immersed in the bath, providing constant stirring of the cells.

Cells. Two Beckman Model CEL-3L-025 conductivity cells were used for all measurements. These were Erlenmeyer flasks with electrodes contained in a sidearm.

Cell constants in water were not entirely reproducible. It is expected, however, that the true cell constant was determined on two successive "good" days. These were determined utilizing Anachemia Ltd., Montreal, primary standard KCl according to the equation of Fuoss[25]: $\Lambda = 149.93 - 94.56C^{1/2} + 58.75C\log C + 198.4C$ where C is the molar concentration of KCl.

Cell constants were also determined in methanol with KCl according to data of Butler, Schiff and Gordon[26]:

$$\frac{\Lambda + 2\sigma C^{1/2}}{1 - \delta C^{1/2}} = \Lambda^{\circ} + BC + EC\log C$$

where C is again molar concentration.

The measured cell constants were:

Cell	Water	Methanol
1	0.29283±0.00002	0.29323±0.00006
2	0.29298±0.00002	0.29333±0.00003

Preparation of Solutions. The stock solutions were prepared by weighing salt on an Ainsworth TCX semimicro balance and adding to a known weight of solvent. All weights were corrected to vacuo.

The solvent was allowed to equilibrate and the resistance was measured. Seven to eight additions of stock solution were made to a known amount of solvent in the cell, allowing equilibration after each addition. Resistance measurements were made at 1000 cycles/sec. and 3000 cycles/sec.

The infinite resistance [R_∞] was calculated by extrapolating a plot of resistance versus $1/f^*$ to infinite frequency.

---

*The "usual" extrapolation versus $1/\sqrt{f}$ showed a wider variation of cell constant with concentration.

The weight dilution method utilized was used since more reproducible results are possible. The solvent correction is for that specific run and day, not just an average of all solvent used. This is most important in the most dilute regions where the solvent contributes up to 10% of the measured resistance.

The density of the stock solutions was taken as that of the solvent since the solutions are in such a dilute region.

RESULTS

Treatment of Raw Data

The resistance meaurements taken at 1000 and 3000 cycles per second were converted, by extrapolation versus 1/f, into infinite frequency resistances [R∞]. The non-corrected weights of the salt, stock solution, initial solvent, and additions of stock solution along with R∞ data were treated by a FORTRAN IV program written for an IBM 360 model 50 computer.

The data were treated as follows to obtain concentration and equivalent conductance data sets for each salt.

$$V \text{ solution} = \frac{\text{Mass of solution [g]}}{\text{Solvent density [g/l]}}$$

At such dilute concentrations, this is a reasonable assumption. Then

$$C \text{ solution [moles/l]} = \frac{\bar{C}_{stock} \text{ [moles/gram]} \times G_{stock} \text{ [gram]}}{V \text{ solution [liter]}}$$

Knowing k, the cell constant from measurements of KCl, one may calculate the specific conductance, L. $L = k/R_\infty$

The specific conductance of the solute may be given by:

$$L_{solute} = L_{solution} - L_{solvent}$$

Utilizing the specific conductance of the solute, L_s, and the normality of the solution, N, one may calculate the equivalent conductance, Λ.

$$\Lambda \text{ [ohm}^{-1}\text{cm}^2\text{equiv}^{-1}\text{]} = 1000\ L_s/N$$

Application of Data to Theory

The Onsager limiting law may be applied to the data to determine whether the salt in the solution is ion-paired or unassociated. It is generally considered that if the experimental curve approaches the limiting law from above, the salt is assumed unassociated. On the other hand, if the experimental curve falls below the limiting law, the salt may be considered associated.

Sodium polymethylene α,ω-disulfonates. Although the reproducibility of the cell contants in water was not acceptable, one run using the sodium ethane disulfonate salt was made. These data are tabulated in Table III. The phoreogram, a Λ versus $\sqrt{C}$ plot, Figure 1, followed the limiting law very closely indicating no association. The higher concentration points do trend upward from the line indicating the breakdown of the limiting law as was expected. This plot allows one to compare the behavior of the salts in methanol, in which the remaining work was completed.

The sodium salts are unsymmetrical 1,2-electrolytes. The Fuoss-Onsager and related treatments cannot be used for these salts since they are limited to symmetrical electrolytes.

The Murphy-Cohen treatment has been formulated for use with unsymmetrical electrolytes of this nature. The equation is

$$\Lambda = \Lambda^\circ - S\sqrt{C} + E'C\ln C + J'C$$

where Λ° is the equivalent conductance at infinite dilutions. Constants S,E and J are the theortical terms defined in Appendix 1. A Λ' versus C

Table III. Sodium Ethane 1,2-Disulfonate in Water Concentration, Equivalent Conductance Data

$CX10^4$	Λ
0.7472	115.959
1.3051	115.137
1.9313	114.531
2.5497	114.029
4.7584	112.771
9.0870	111.417
16.8493	110.127
	Λ_o= 117.695

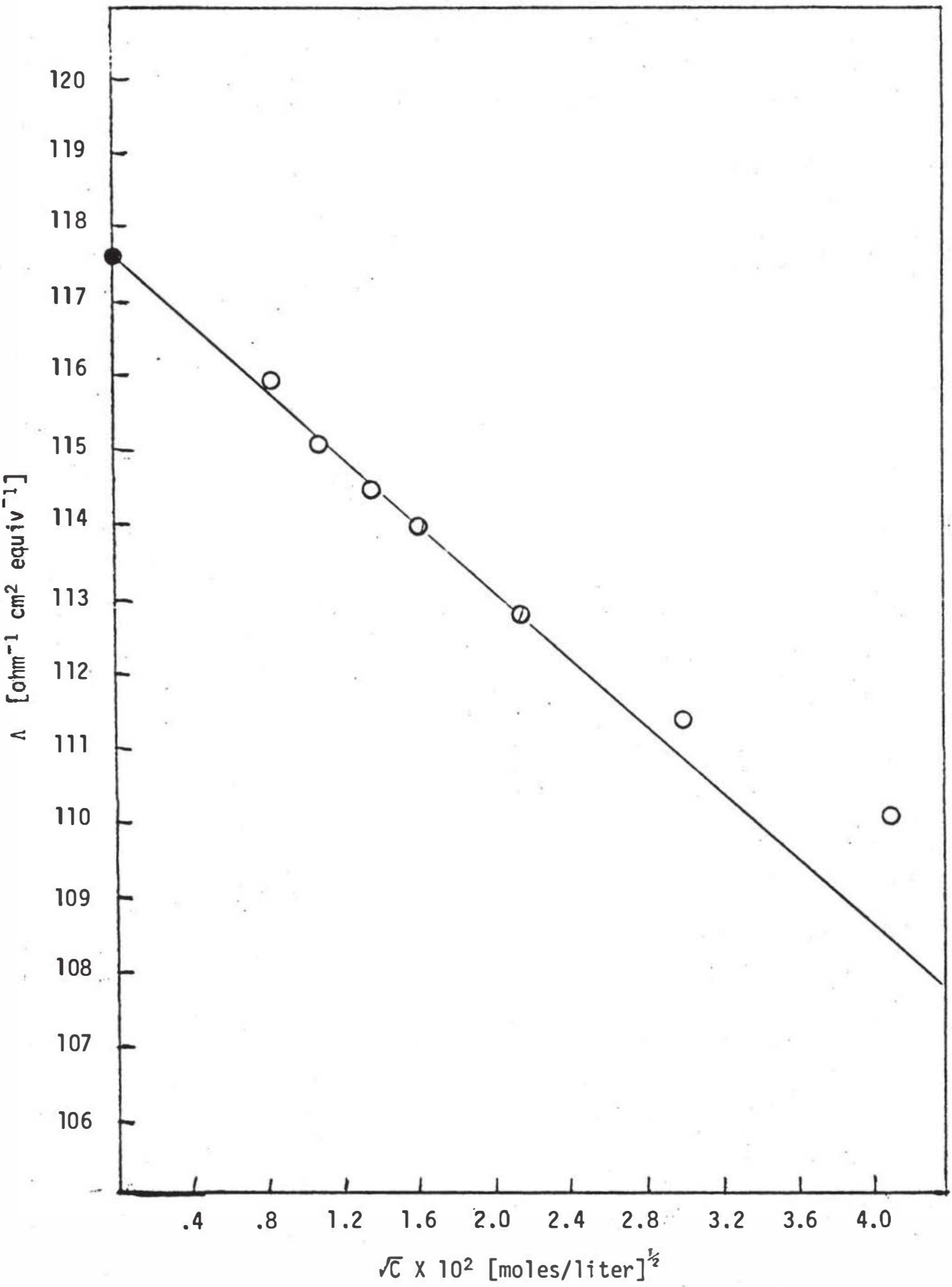

Figure 1. Sodium Ethane 1,2-Disulfonate in Water.

plot evalutes Λ° and J where

$$\Lambda' = \Lambda + S\sqrt{C} - E'C\ln C = \Lambda_o + J'C$$

The intercept of the plot is Λ_o with the slope J. The new Λ_o gives a better Λ' and hence a better Λ_o and J. This iterative technique repeats until Λ_o and J converge. The details of the computer program may be found in Appendix 2.

The concentration and equivalent conductance data for the sodium salts may be seen in Table IV. The phoreograms, Figures 2-7, of the sodium salts are seen to lie below the limiting law. The limiting law is indicated by the dashed line while the circles indicate the points as determined by the Murphy-Cohen equation.

This deviation may be explained as some probable association or possible failure of the limiting law. This may be expected in solvents of low dielectric constant.

In each salt, the lowest two or three points lie on or near the limiting law within experimental error. The Λ_o values are taken to be correct since a line to the Λ_o value may be drawn through the aforementioned points.

A plot of Λ' versus C as determined by the Murphy-Cohen equation, Figure 8, should be a straight line from which Λ_o and J may be determined. It is readily apparent upon examination that this is not the case. The final two or three points tend to curve up from the projected line. This deviation at high concentration possibly indicates a breakdown of the theory in this range.

As noted previously, however, the lowest concentrations do seem to give the correct Λ_o value as does the phoreogram.

Table IV. Sodium Polymethylene α,ω-Disulfonates in Methanol
Concentration, Equivalent Conductance Data

$Na_2(SO_3)_2(CH_2)_2$

C X 10^4	Λ
0.3289	103.018
0.3289	101.010
1.1475	98.641
1.7882	95.840
2.1940	94.322
2.7563	92.516
3.1874	91.263
3.5176	90.374

Λ_o = 107.465

$Na_2(SO_3)_2(CH_2)_3$

C X 10^4	Λ
0.3586	99.497
0.5920	98.075
1.0504	95.503
1.5985	92.997
2.1310	90.983
2.6673	89.236
2.9089	88.523

Λ_o = 104.155

$Na_2(SO_3)_2(CH_2)_4$

C X 10^4	Λ
0.4381	97.481
0.8320	95.530
1.6247	92.264
2.0764	90.765
2.4521	89.603
2.7585	88.743
3.1627	87.702

Λ_o = 102.478

$Na_2(SO_3)_2(CH_2)_5$

C X 10^4	Λ
0.4416	96.360
0.8177	94.945
1.5944	91.957
2.0807	90.441
2.4270	89.462
2.7366	88.656
3.0826	87.823

Λ_o = 101.391

Table IV. [Continued]

$Na_2(SO_3)_2(CH_2)_6$

CXCO^4	Λ	CX10^4	Λ
0.4676	92.045	0.3361	95.018
0.9257	90.484	0.6502	93.114
1.5170	88.489	1.0832	91.183
2.0971	86.805	1.6972	88.953
2.5651	85.594	2.3222	87.089
3.0417	84.502	2.8576	85.233
3.6947	83.181	3.4413	84.430
	Λ_o= 98.350	4.3985	82.574
			Λ_o = 100.200

$Na_2(SO_3)_2(CH_2)_{10}$

CX10^4	Λ	CX10^4	Λ
0.5043	93.275	0.4238	93.700
0.9493	91.491	0.7413	91.876
1.4153	89.618	1.0461	90.479
2.0099	87.535	1.5575	88.572
2.4031	86.304	2.0323	87.070
2.8290	85.076	2.4429	85.927
3.3452	83.756	3.0514	84.408
		4.6630	81.134
	Λ_o = 99.680		Λ_o = 100.500

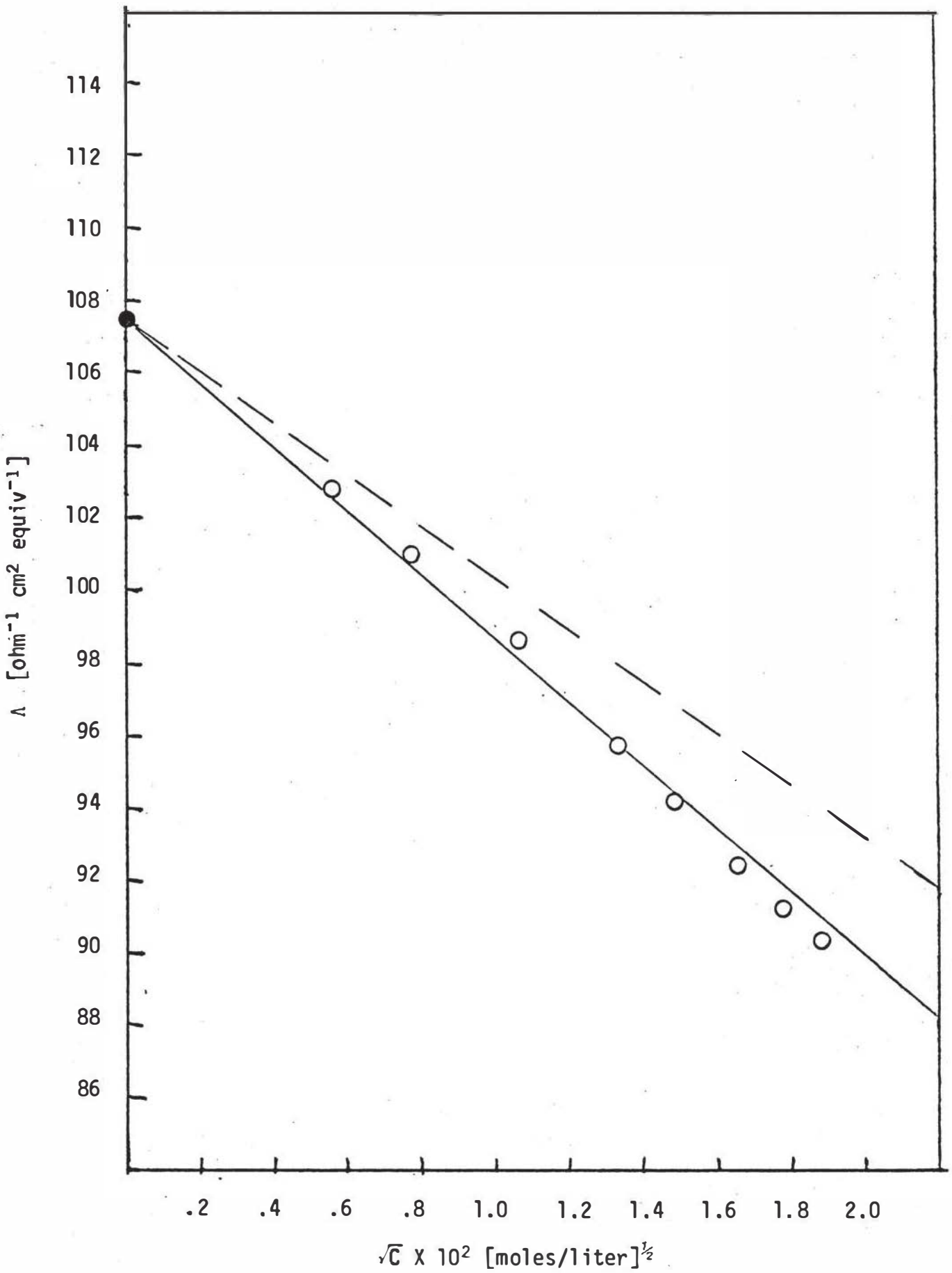

Figure 2. Typical Phoreogram [Sodium Ethane 1,2-Oisulfonate in Methanol] No association indicated.

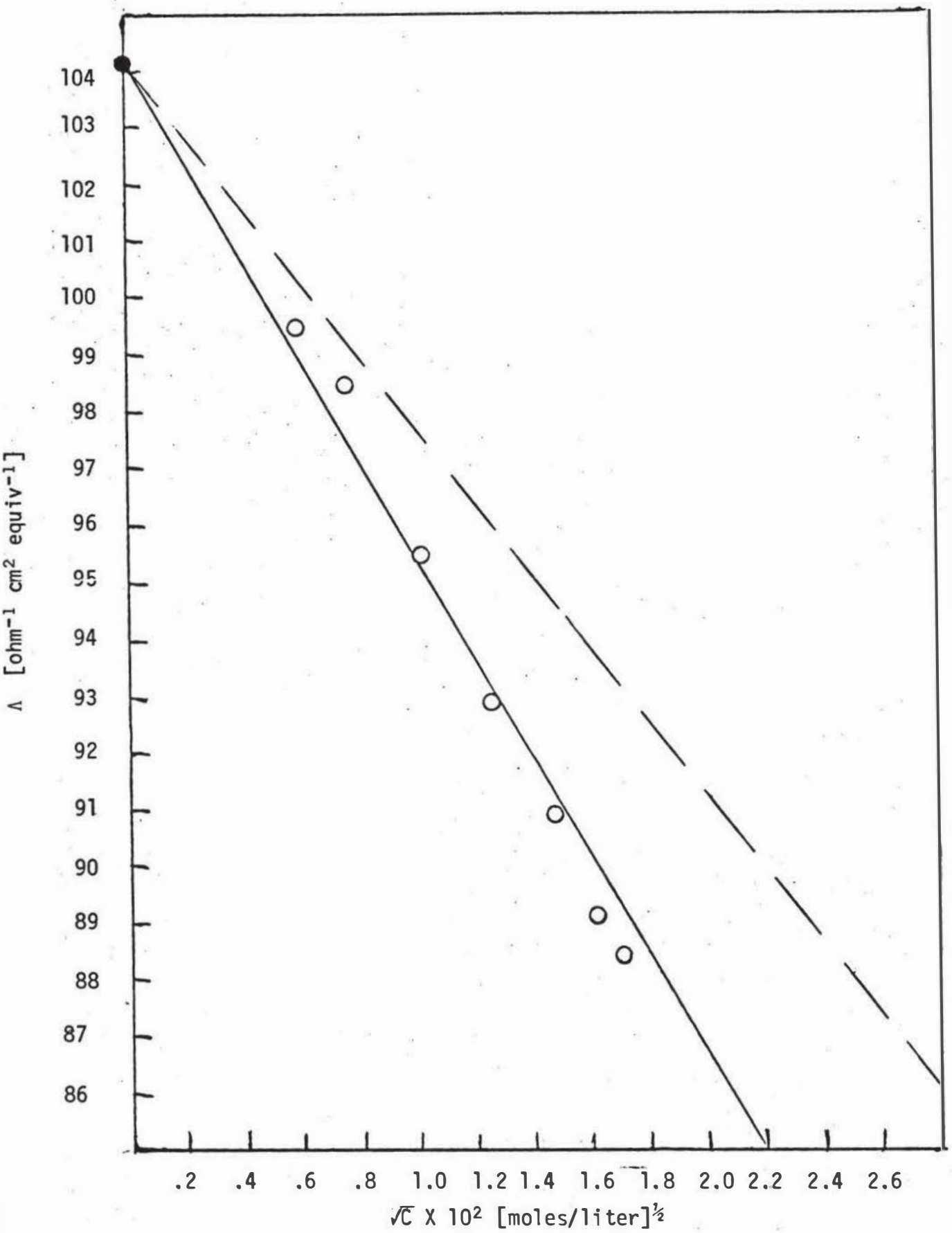

Figure 3. Sodium Propane 1,3-Disulfonate in Methanol.

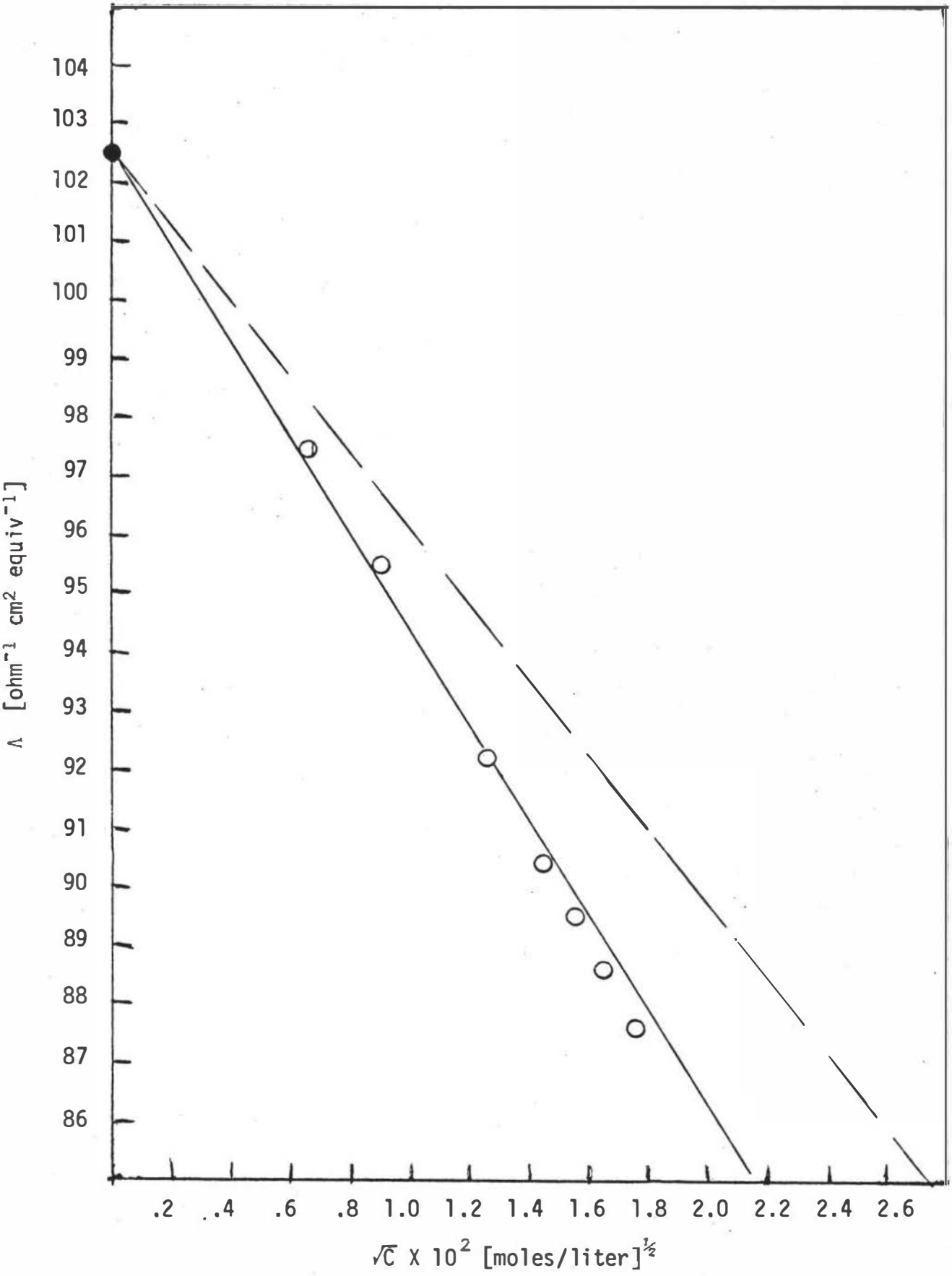

Figure 4. Sodium Butane 1,4-Disulfonate in Methanol.

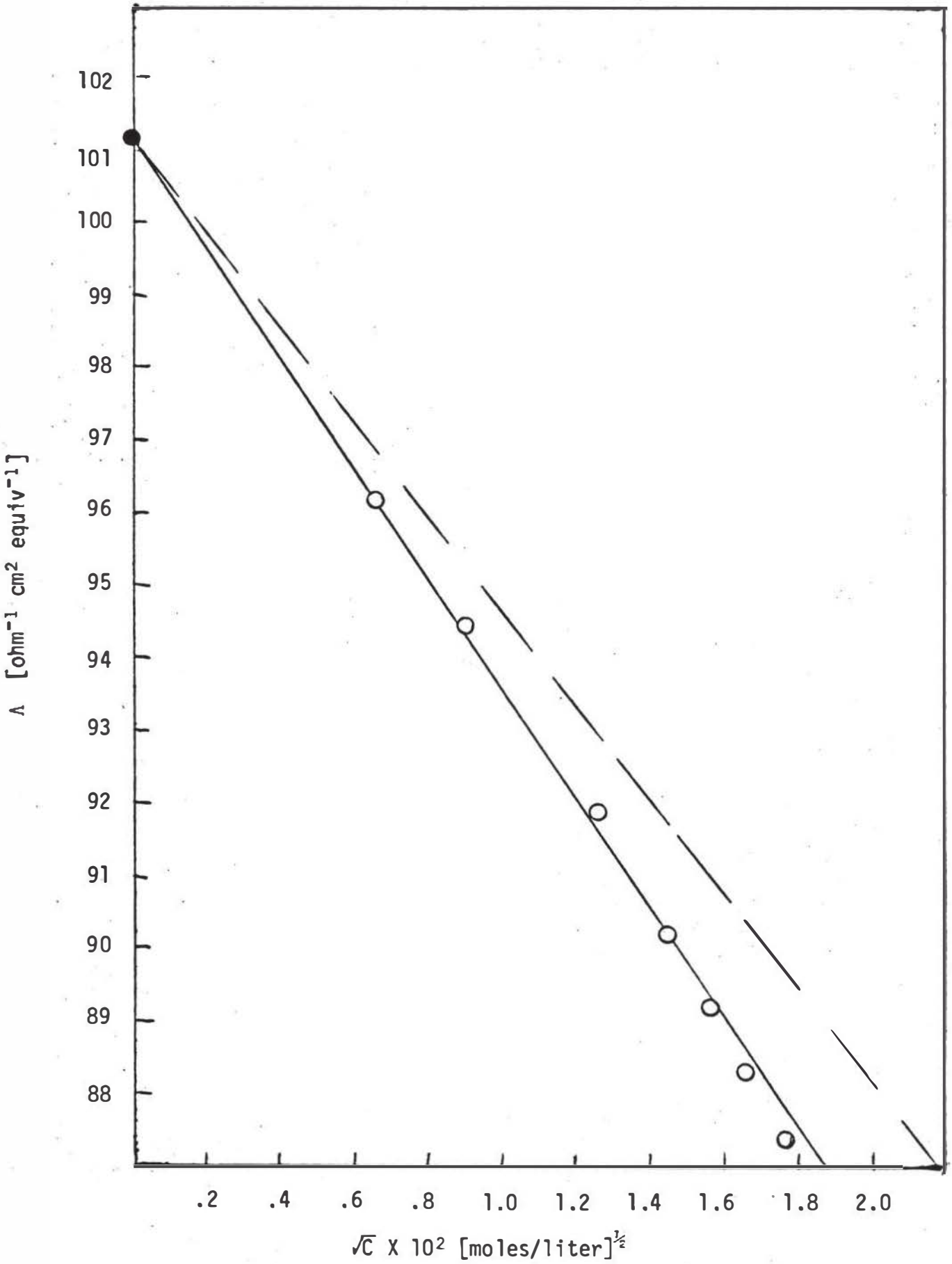

Figure 5. Sodium Pentane 1,5-Disulfonate in Methanol.

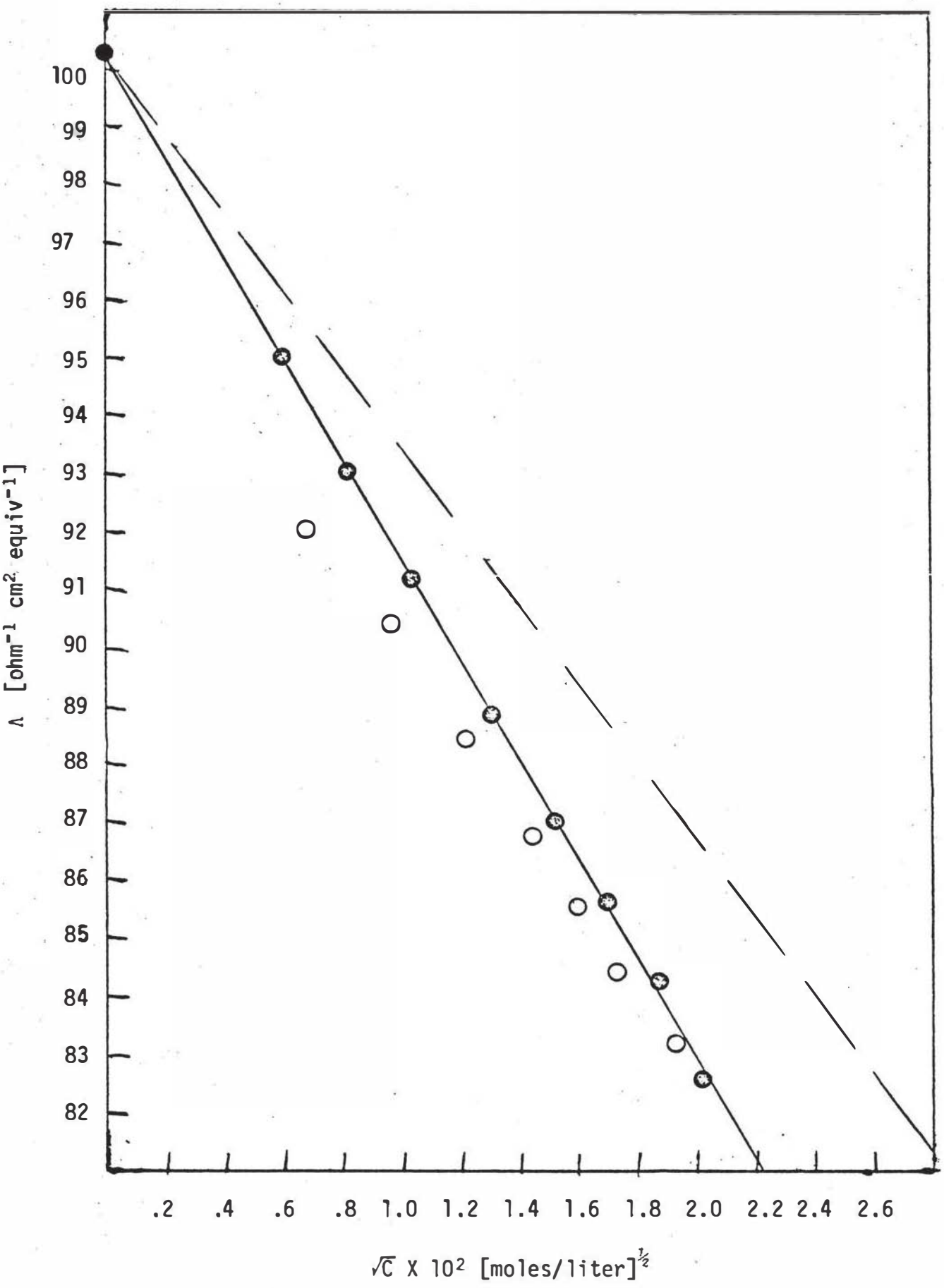

Figure 6. Sodium Hexane 1,6-Disulfonate in Methanol.

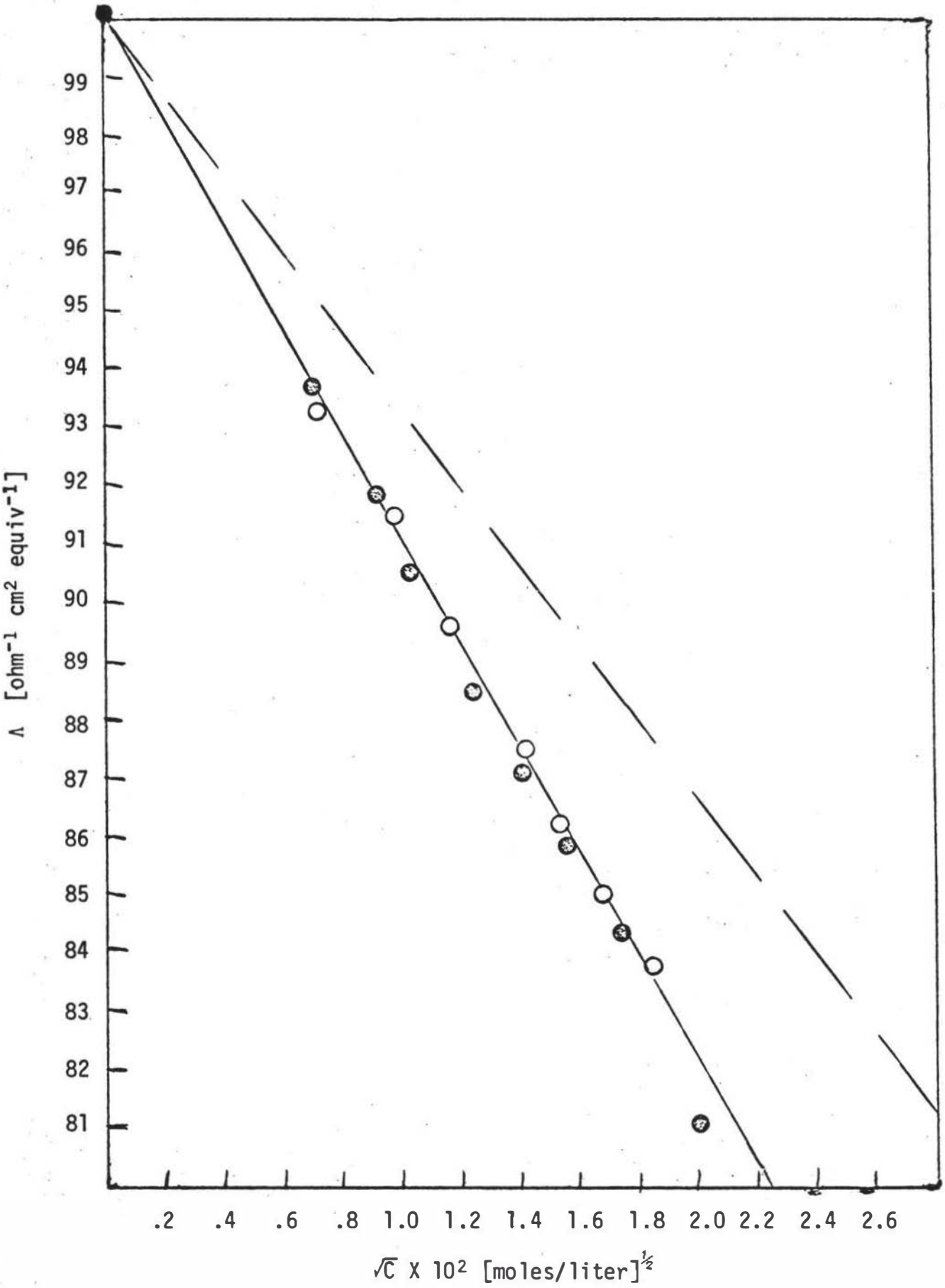

Figure 7. Sodium Decane 1,10-Disulfonate in Methanol.

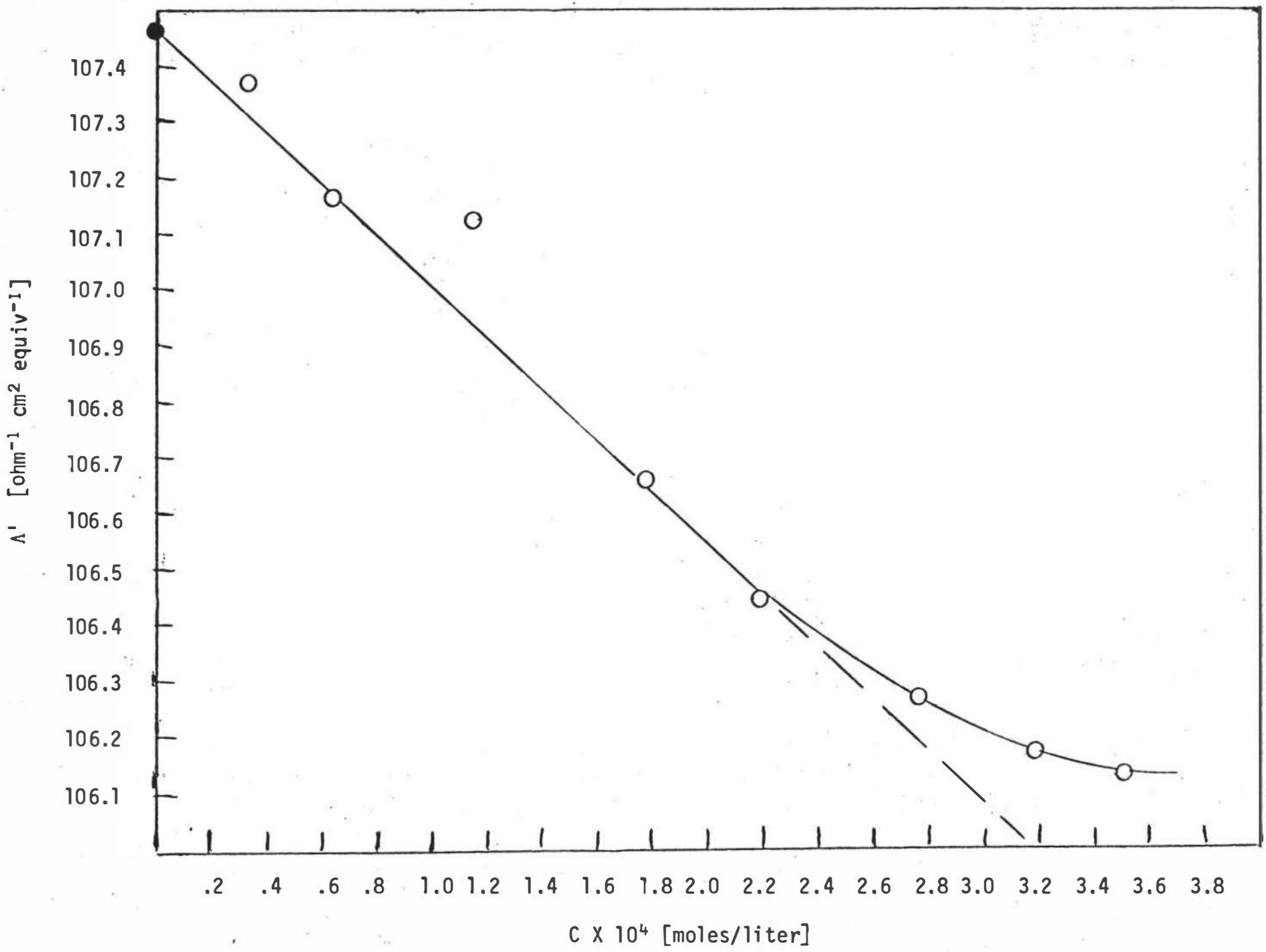

Figure 8. Λ' versus C [Sample plot for determination of Λ° and J by Murphy-Cohen Equation; sodium ethane salt]

Of particular interest, is the near equality of the Λ_o values for the sodium salts of the hexane and decane disulfonates. A plot of Λ_o versus z was made, Figure 9. A non-linear plot is obtained where a definite leveling of the curve is observed from z = 6 to z = 10.

The addition of a methylene group to the molecule of sodium ethane disulfonate tends to change the characteristic of the molecule to a greater degree than would a similar addition to the larger sodium hexane disulfonate molecule. This consideration would rationalize the decline in the slope of the line as the degree of polymerization increases.

Magnesium polymethylene α,ω disulfonates. The symmetrical, 2-2, electrolytes showed a high degree of association as indicated by Figure 10. The data for the salts may be seen in Table V.

An attempt was made to use the Murphy-Cohen equation to determine the Λ_o and K_A of these salts. It was found, however, that the association was so great that no meaningful values could be obtained.

Kohlrausch's law, $\Lambda_o = \lambda^+ + \lambda^-$, was utilized to obtain Λ_o values. The value of $\lambda^+_{Mg} = 49.$ was obtained from the literature[27] and the values calculated for the anion from the sodium salt determinations were used, Table VII.

Since the Λ_o versus $\sqrt{C}$ phoreograms showed association and were thought to be similar to that of acetic acid, the following data treatment was used to obtain apparent association constants K'_A.

$$\alpha = \frac{\Lambda}{\Lambda} \qquad \alpha = \text{degree of dissociation}$$

$$K'_A = \frac{(1 - \alpha)}{\alpha^2 C}$$

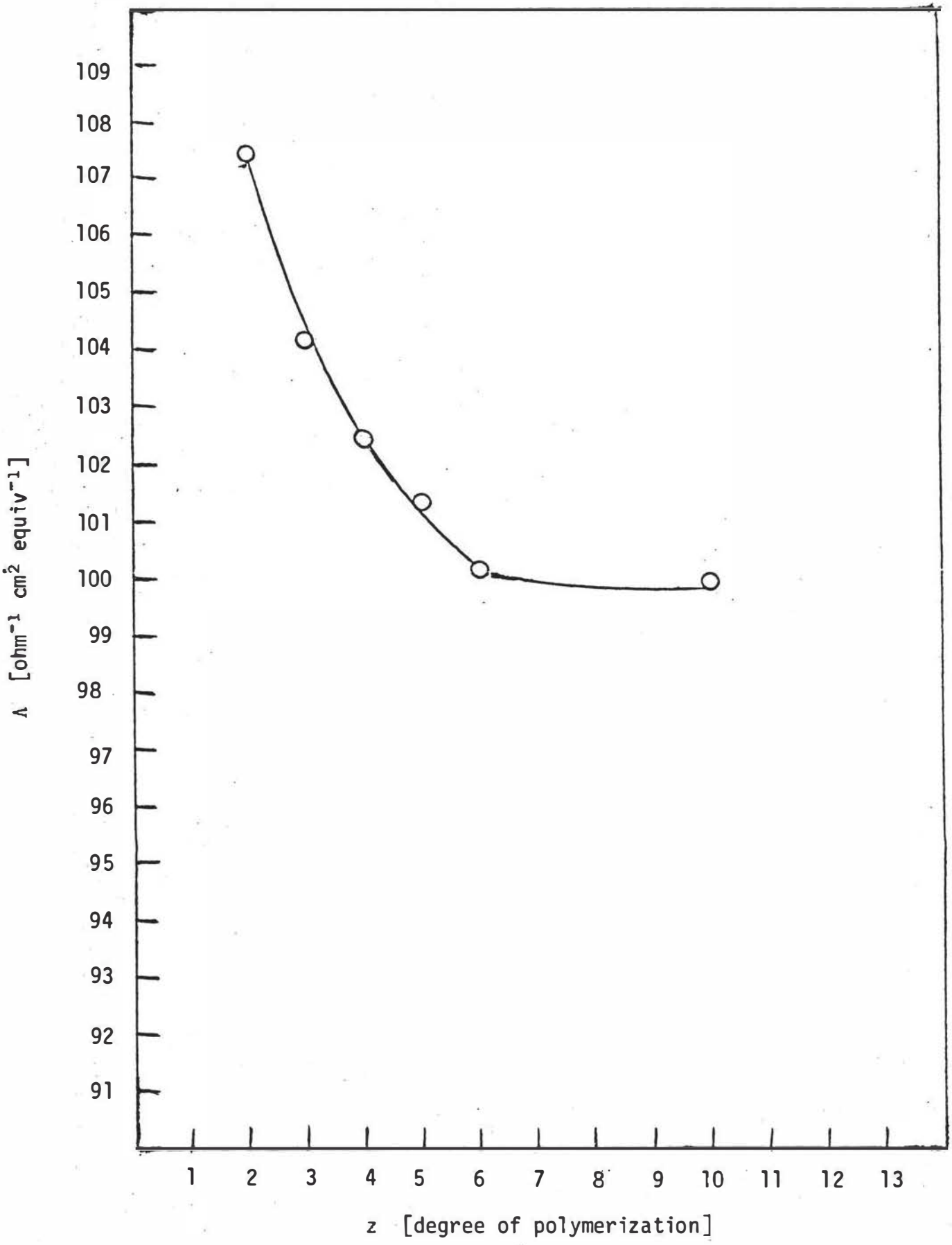

Figure 9. Λ_o vs. z [Λ_o values for sodium salt data in methanol].

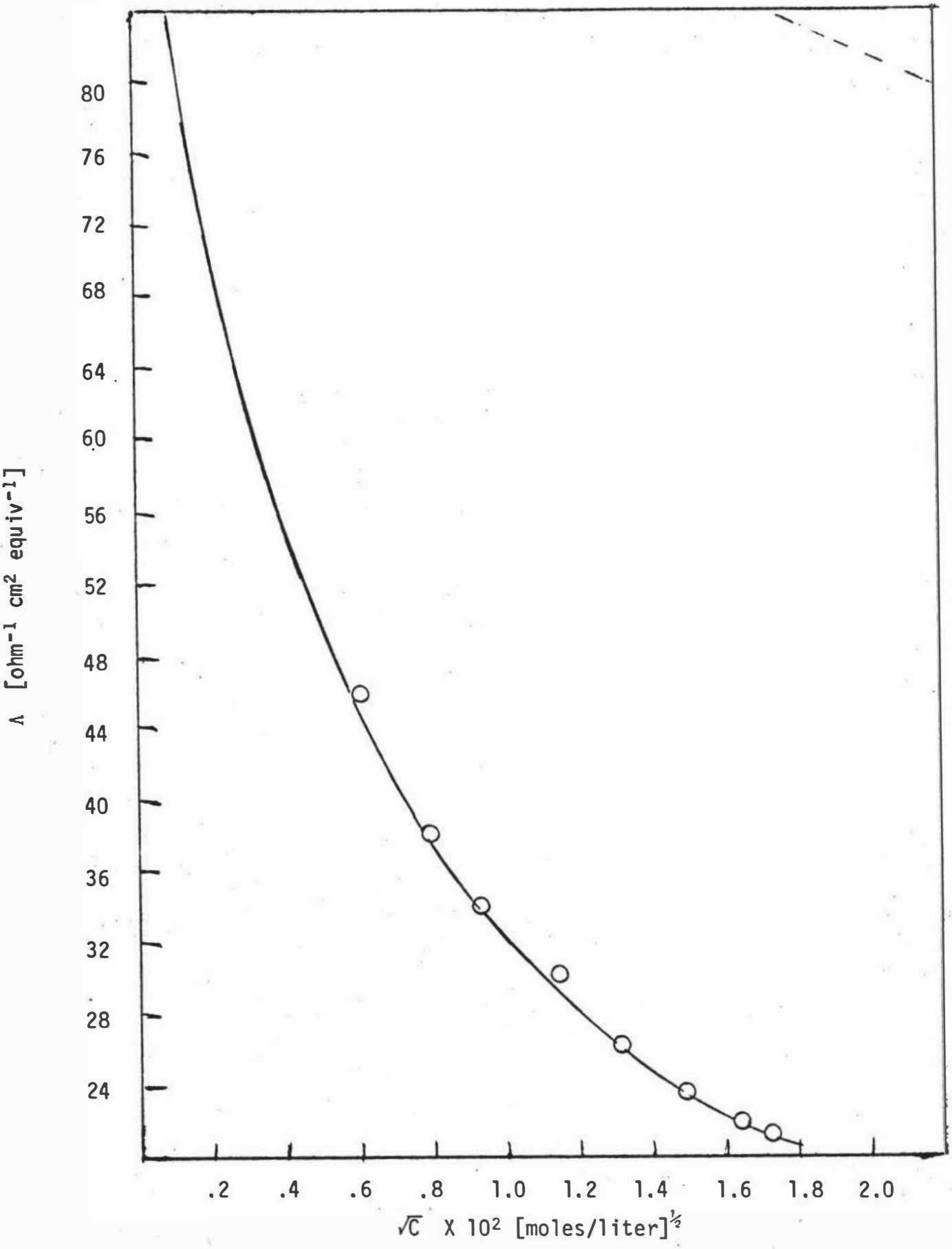

Figure 10. Typical Phoreogram [Magnesium Ethane 1,2-Disulfonate in Methanol] Association indicated.

Table V. Magnesium Polymethylene α,ω-Disulfonates in Methanol Concentration, Equivalent Conductance Data

$Mg(SO_3)_2(CH_2)_2$

$CX10^4$	Λ
0.3710	45.966
0.6362	38.231
0.8729	34.104
1.3111	29.312
1.7295	26.376
2.2441	23.855
2.7178	22.141
2.9558	21.402

$Mg(SO_3)_2(CH_2)_3$

$CX10^4$	Λ
0.5398	42.529
0.9865	35.489
1.5829	30.775
2.1031	28.272
2.6247	26.497
3.0263	25.437
3.4125	24.587
3.8373	23.788

$Mg(SO_3)_2(CH_2)_4$

$CX10^4$	Λ
0.5285	49.073
0.9580	42.068
1.5890	36.792
2.0596	34.343
2.6285	32.213
3.0750	30.880
3.5086	29.910
3.8585	29.197

$Mg(SO_3)_2(CH_2)_5$

$CX10^4$	Λ
0.5214	56.878
1.0624	46.479
1.5049	41.615
1.9651	38.172
2.5514	35.072
3.0216	33.170
3.3288	32.131
3.7182	30.975

Table V. [Continued]

$Mg(SO_3)_2(CH_2)_6$		$Mg(SO_3)_2(CH_2)_{10}$	
$CX10^4$	Λ	$CX10^4$	Λ
0.3364	65.767	0.3908	66.829
0.7014	54.080	0.7168	58.216
1.0126	48.511	0.9998	53.424
1.5570	44.408	1.5783	47.053
2.2354	37.686	2.2952	42.121
2.0630	35.823	2.6929	40.120
3.1266	33.688	3.2438	37.869
4.5795	29.609	4.7613	33.569

A plot of log K_A' versus $\sqrt{C}$ extrapolated to infinite dilution yields the K_A from the antilog of the intercept. Values of K_A for each salt have been determined and are tabulated in Table VI. Representative plots of log K_A' versus $\sqrt{C}$ have been prepared for the ethane and decane salts, Figures 11 and 12.

The deviation from linearity of the higher concentration points is due to activity coefficient effects. These can only be assumed to be negligible in very dilute solutions.

The values of K_A can be seen to decrease monotonically as the chain length of the salt increases. This may be explained by charge separation considerations. As the charge separation increases the charge density on the anion decreases, which causes a corresponding decrease in ion-ion interaction. A plot of log K_A versus chain length, Figure 13, shows this trend rather effectively. The greatest change occurs between the butane and pentane where the charge density is apparently changing its nature from a delocalized charge over the chain, to two semi-localized charge centers. This seems to be an increasing trend until the chain length reaches 8 to 10 where the charges might be completely separated or acting nearly independently.

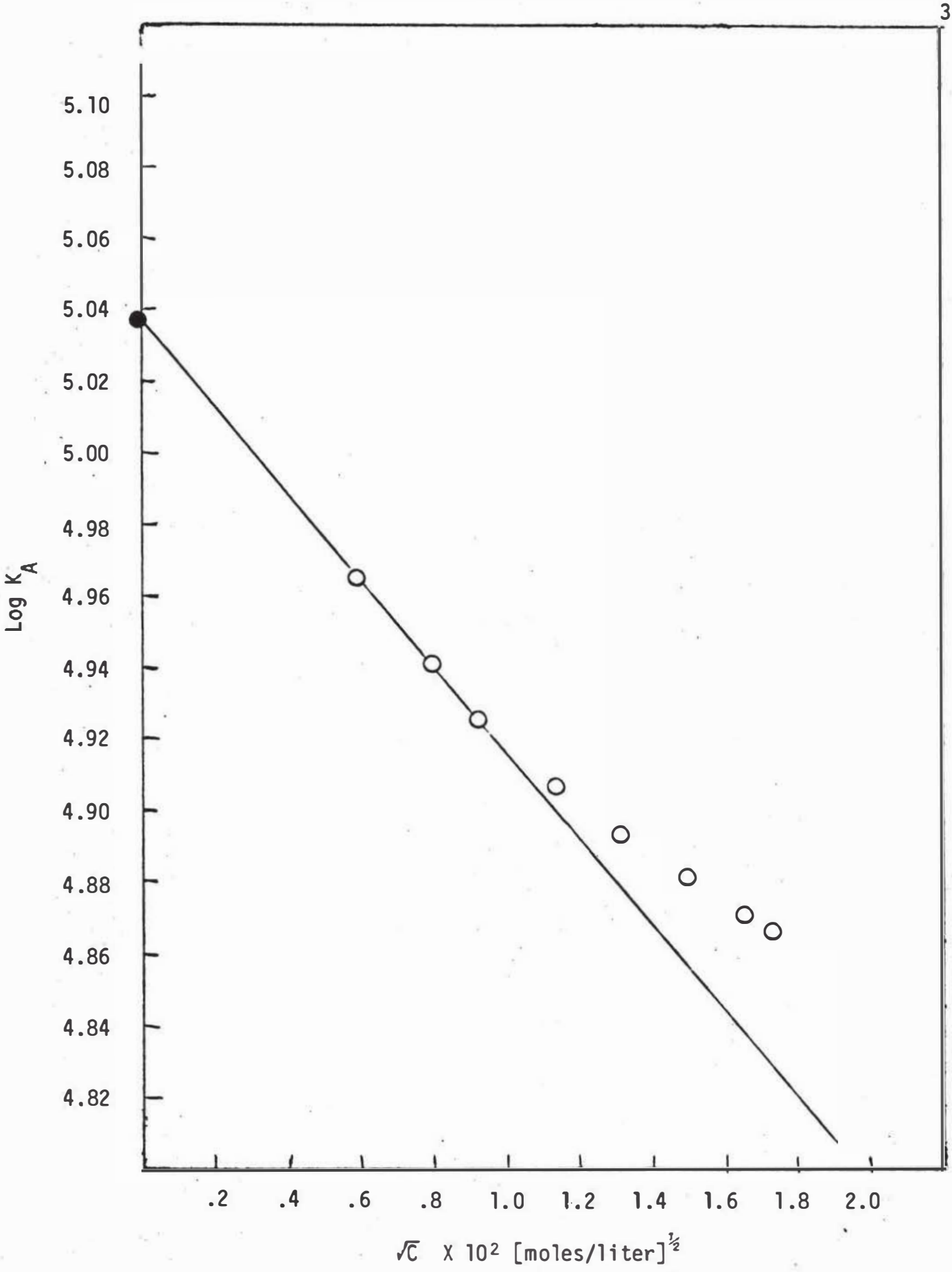

Figure 11. Log K_A versus $\sqrt{C}$ [Magnesium Ethane 1,2-Disulfonate in Methanol].

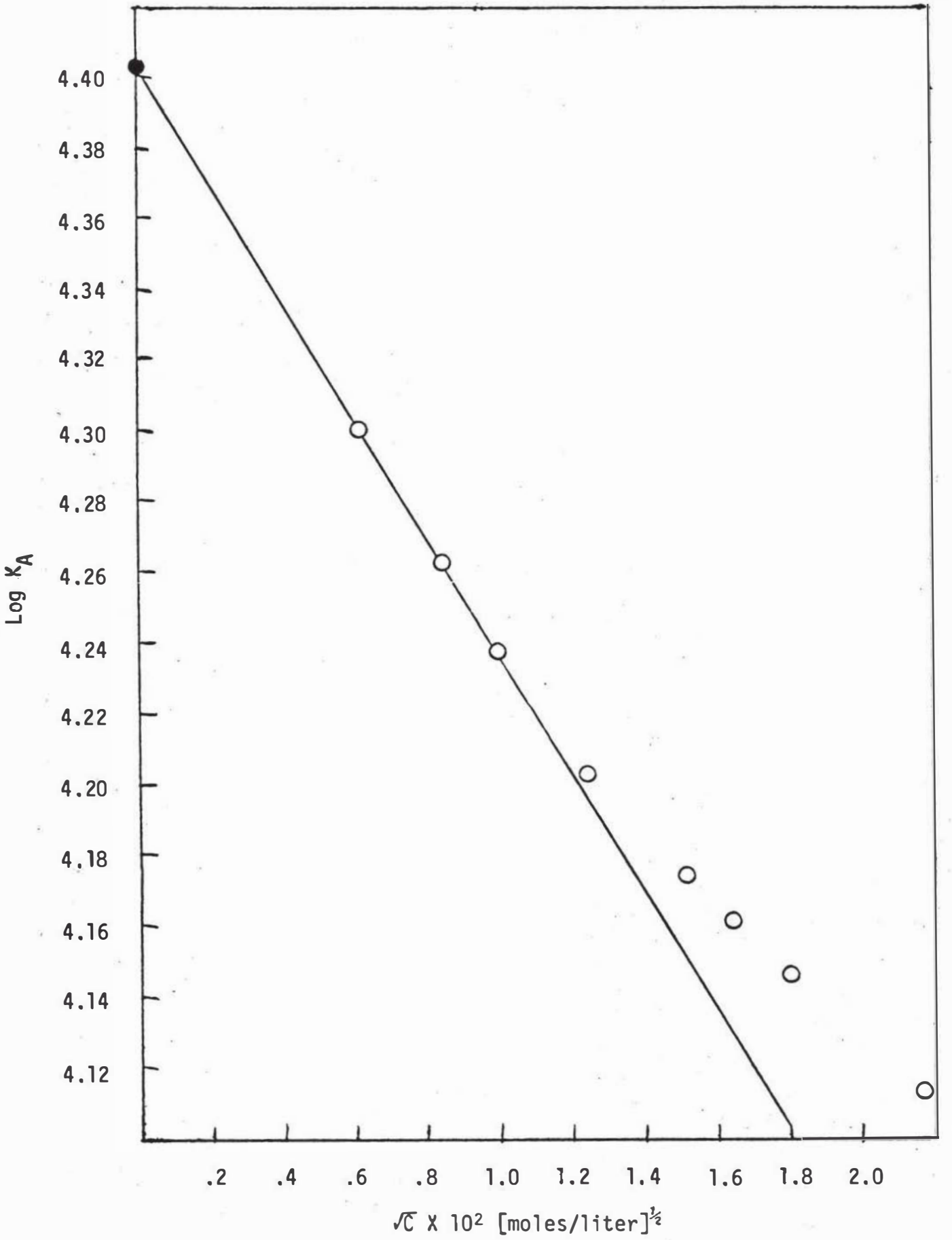

Figure 12. Log K_A versus $\sqrt{C}$ [Magnesium Decane 1, 10-Disulfonate in Methanol].

Table VI. Calculated Association Constants

$Mg(SO_3)_2(CH_2)_n$	log K_A	K_A
n		
2	5.0370	108,950
3	5.0100	102,330
4	4.8880	77,270
5	4.6000	39,810
6	4.5070	32,140
10	4.4020	25,260

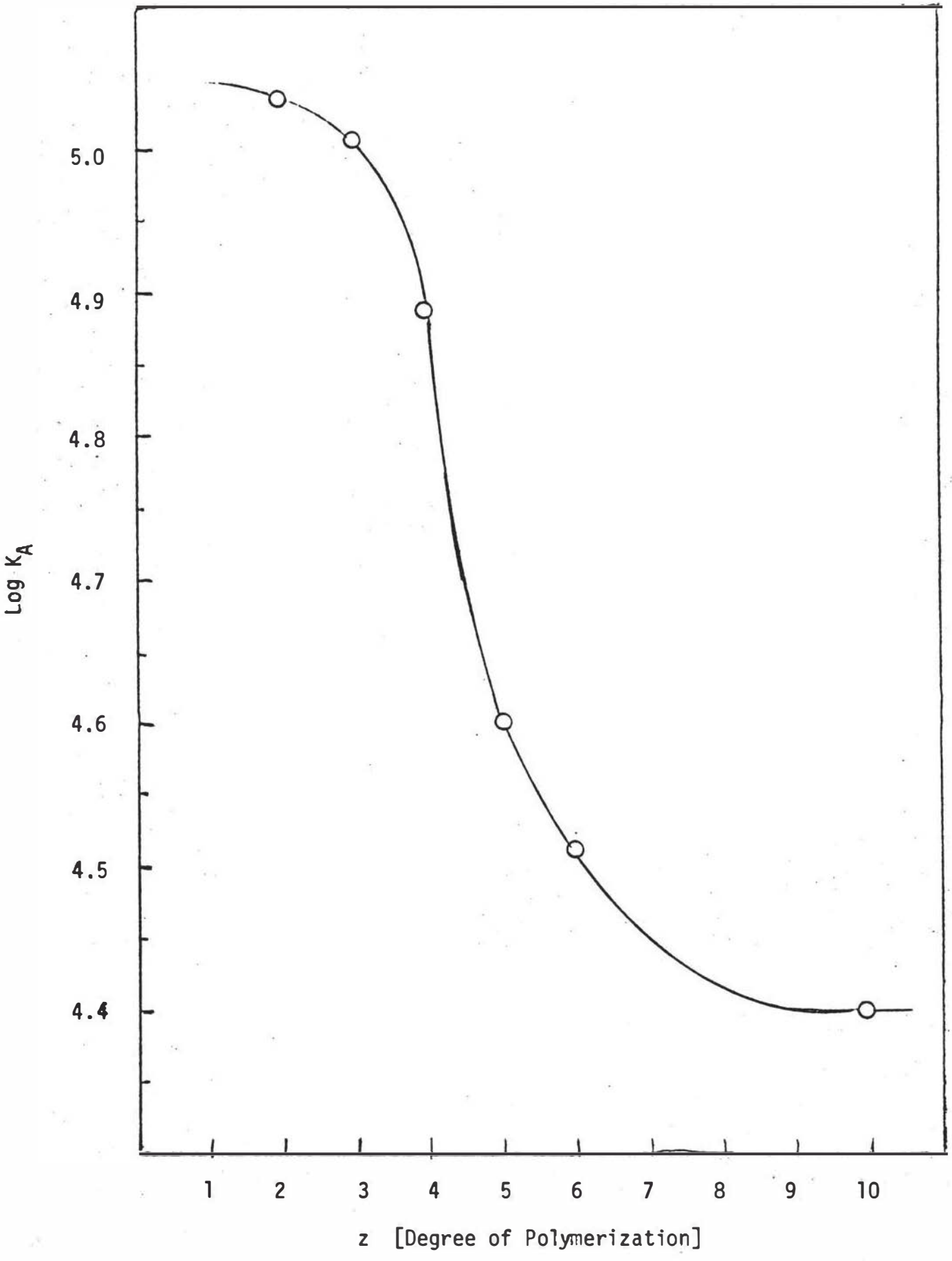

Figure 13. Log K_A versus z [Magnesium salts in Methanol]

Table VII. Conductance Parameters

$Na_2(SO_3)_2(CH_2)_n$	-in Methanol		-in Water	
n	Λ_o	λ_o^{-}(a	λ_o^{+}	λ_o^{-}(a
2	107.465	62.245	117.695	67.605
3	104.155	58.935		
4	102.478	57.258		
5	101.391	56.258		
6	100.200	54.98		
10	100.090(b	54.81		

a) λ°_{Na} = 45.22, λ°_{Na} = 50.090: in Methanol, in Water (taken from Harned and Owen, reference [28])

b) average value

$Mg(SO_3)_2(CH_2)_n$	in Methanol	
n	Λ_o	K_A
2	111.25	108,950
3	107.94	102,330
4	106.26	77,270
5	105.17	39,810
6	103.98	32,140
10	101.85	25,260

Frictional Coefficients. The experimentally determined equivalent conductancesof the anions, Table VII, were used to calculate the frictional coefficients from the formula

$$\zeta = \frac{96494|Z_i|e}{300\,\lambda_i}$$

These values when plotted versus degree of polymerization, follow a curve which increases to a plateau as the chain length increases to z=10. By fixing the parameter ζ_o one may calculate the value of ζ for the Peterlin rod and bead model. Peterlin has calculated values of ζ_o/ζ for values of z=1 to z=100. The value obtained from the graph, ζ/ζ_o, versus z, Figure 14, may be used to calculate the ζ of the derived salt, Table VIII. Agreement of the experimentally determined ζ's and those calculated from theory are excellent. Plots of ζ versus z for $\zeta_{experiment}$ and ζ_{theory}, Figure 15, show similar curvature and lie on nearly the same line. The decane salt is the only point which deviates substantially from the experimentally determined curve. Since the value of ζ_o was fixed using the $\bar{\lambda_o}$ for the pentane salt, z=5, an intersection of the two lines occurs as would be expected.

The ratio of a/b[hydrodynamic radius of the i th ion a to the interbead b] is representative of the strongest hydrodynamic interaction which requires the elementary spheres to be in contact. The choice of a/b = 0.2 or 0.0 has little effect on the ζ/ζ_o plot at such low values of z[1-10]. See Figure 14.

The value of θ is a measure of the valence angle between the beads of the chain. See Figure 16. The cosine of this angle may then be said to be a measure of the flexibility or rigidity of the chain. The value of cos θ = 1.0 indicates the most rigid chain while cos θ = 0.0

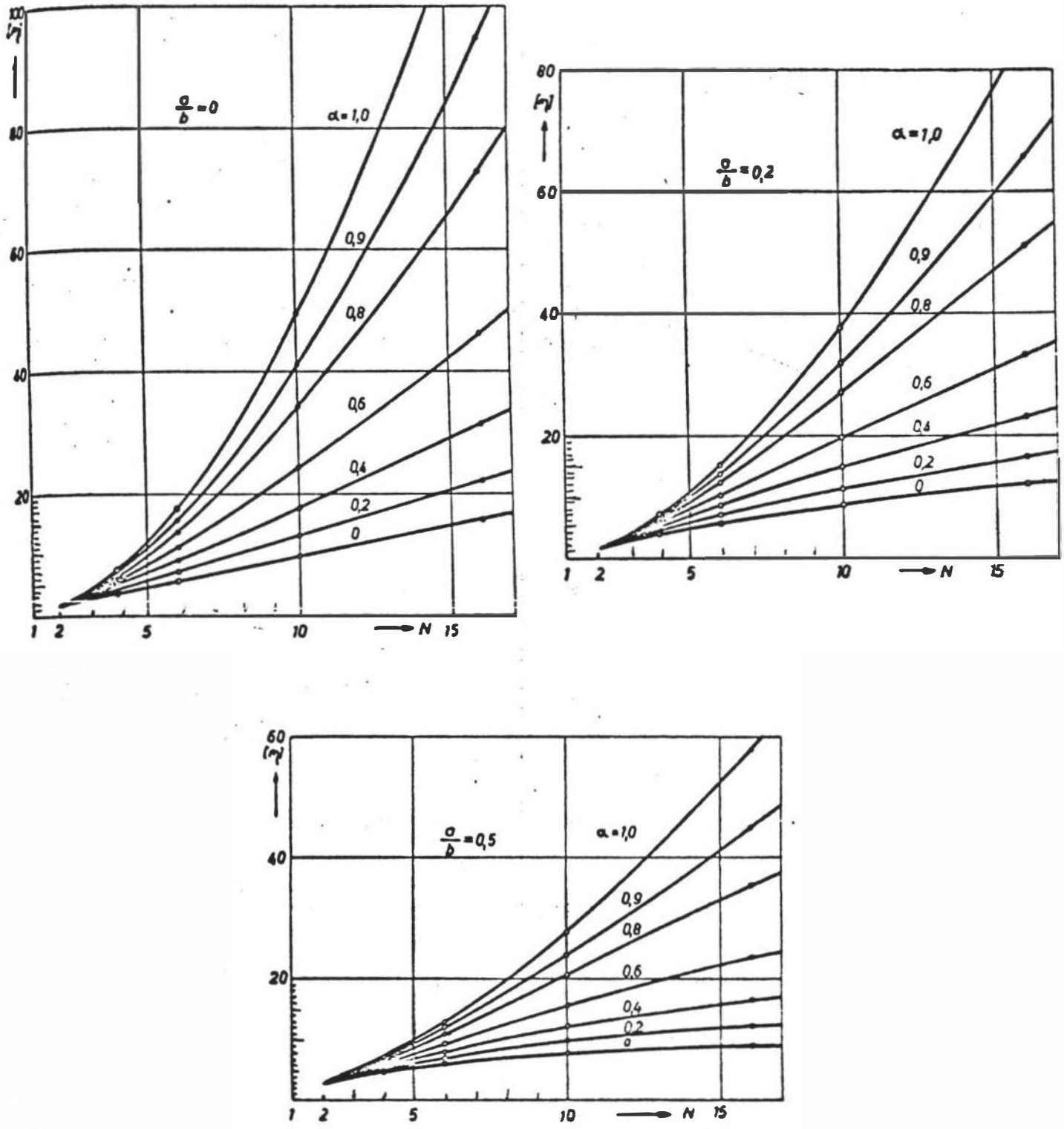

Figure 14. Plots of ζ/ζ_o versus z as calculated by Peterlin*.

*Reprint from A. Peterlin, J. Chim. Phys. 47, 7-8, 669 [1950].

Table VIII. Frictional Coefficients for Peterlin Rod and Bead Model

$Na_2(SO_3)_2(CH_2)_n$	ζ_{exp} (X 10^7 g sec^{-1})	$\zeta^{(a}_{theory}$ (X 10^7 g sec^{-1})	$\bar{\lambda}_{exp}$	$\bar{\lambda}_{theory}$
n				
2	.0496	.0491	62.245	62.89
3	.0524	.0524	58.935	58.96
4	.0539	.0540	57.258	57.18
5	.0549	.0549	56.126	56.13
6	.0562	.0558	54.98	55.49
10	.0563	.0530	54.87	58.23

a) a/b = 0.5, cos θ = 0.5, fix a with $\bar{\lambda}_{exp}$ from pentane (bond angle = 120°)

$Na_2(SO_3)_2(CH_2)_n$	ζ_{exp} (X 10^7 (g/sec))	$\zeta^{(b}_{theory}$ (X 10^7 (g/sec))	$\zeta^{(c}_{theory}$ (X 10^7 (g/sec))
n			
2	.0497	.0573	.0404
3	.0524	.0511	.0431
4	.0539	.0573	.0527
5.	.0549	.0550	.0550
6	.0562	.0512	.0566
10	.0563	.0344	.0674

b) a/b = 0.5, cos θ = .2 (flexible chain) (bond angle = 101.5°)

c) a/b = o.5, cos θ = .8 (rigid chain) (bond angle = 143.0°)

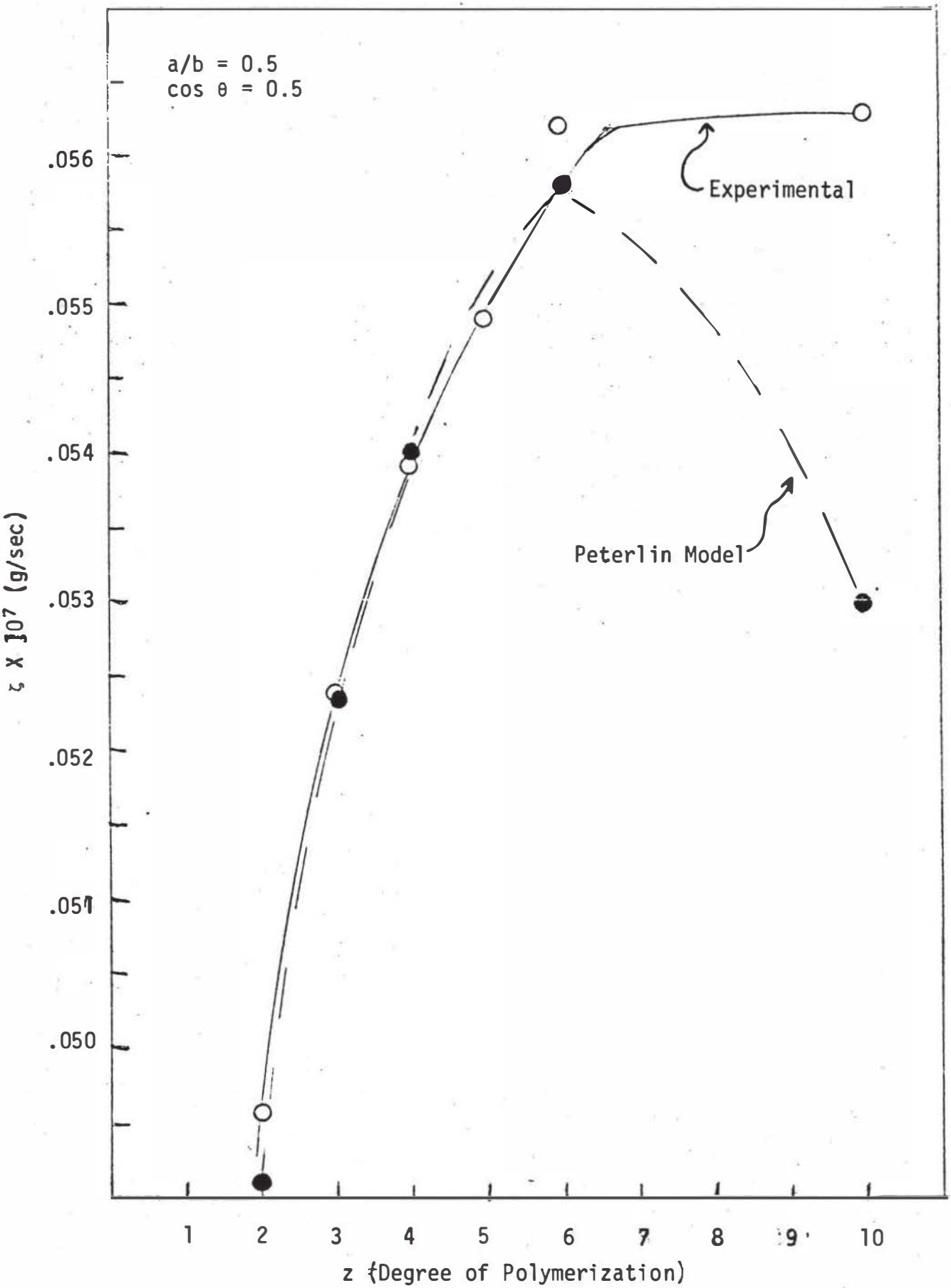

Figure 15. Plot of ζ versus z

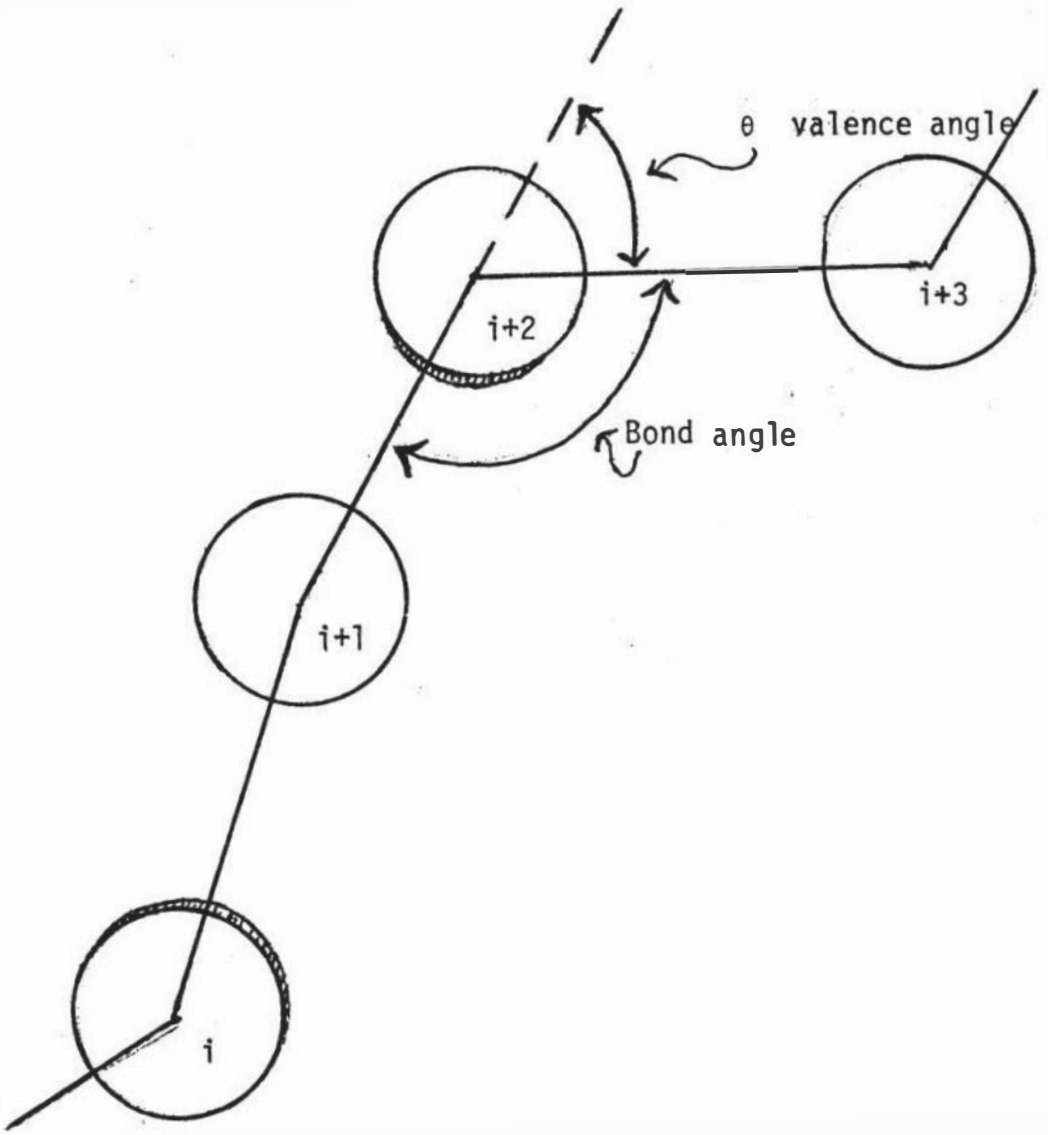

Figure 16. Pictorial Representation of Peterlin Rod and Bead Model.

indicates a maxium flexibility in the chain. The cos θ = 0.5 indicates an intermediate situation corresponding to a moderate barrier of rotation. Plots of ζ versus z for cos θ = 0.2, Figure 17, and cos θ = 0.8, Figure 18, have been made utilizing the same criteria as above. For the plot, cos θ = 0.2, it is easily seen that this does not adequately describe the behavior of the frictional interaction for the long chain decane salt. This is satisfying since one would not predict this molecule to be extremely flexible, though some coiling of the chain would be expected. For the plot when cos θ = 0.8, a deviation above the experimental line is seen in the decane salt. Comparison of this value with that of the plot for cos θ = 0.5 would lead one to "guesstimate" that the true cosine value would be approximately 0.65 to describe the decane salt frictional coefficient adequately. This would correspond to a valence or bond angle of about 131°C. A better approximation of the decane might be a rod like model which would also allow coiling.

Note that the values of ζ for the smaller homologs of the series do not vary as greatly with change in bond angle as the decane salt. This is as expected since coiling does not play an important part until the chain attains a length of five. The greatest deterrant to coiling at lengths z = 5 and 6 would possibly be the highly negative charge in the region of the bulky sulfonate groups.

An alternate theory might be used to calculate ζ, the Perrin rigid ellipsoid model. The value of a' [semi-minor axis] was fixed utilizing the $\zeta_{experiment}$ for z = 5. The value of b' [semi-major axis] was determined by measurements on accurate Hirschfelder models. The distances are listed in Table IX. Once the a' parameter is calculated, a series of ζ may be obtained, Table X. A plot of ζ versus z,

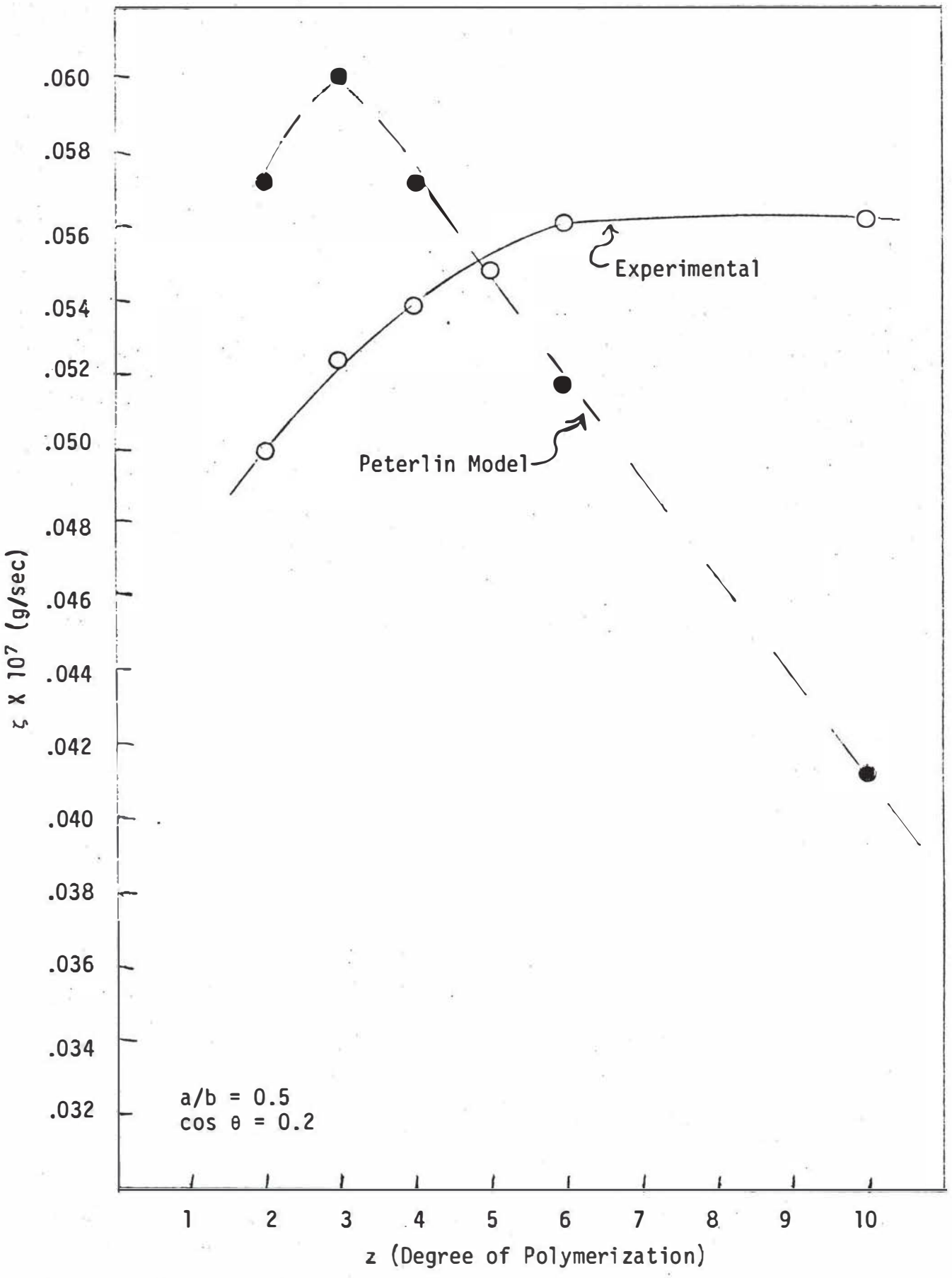

Figure 17. Plot of ζ versus z.

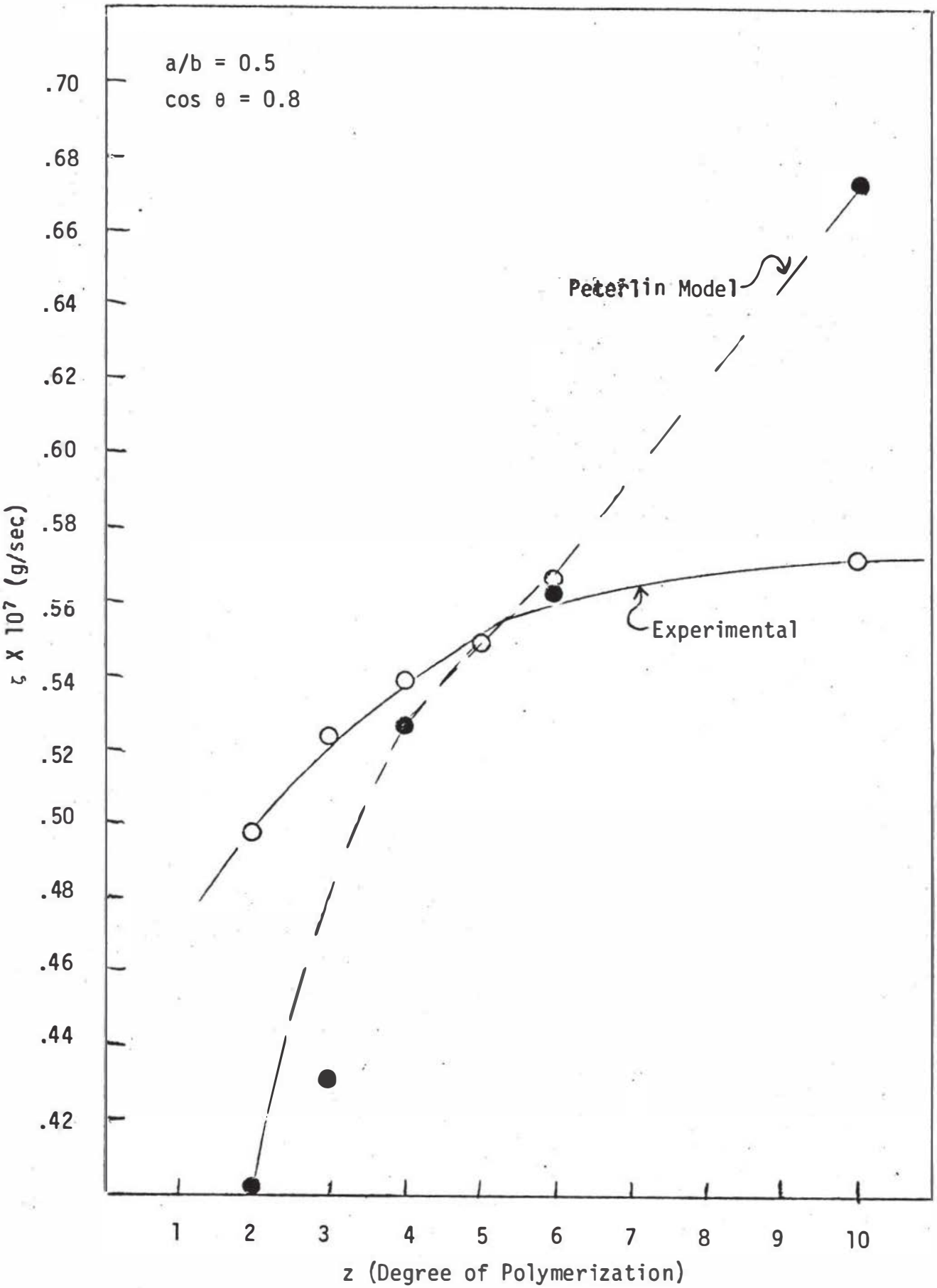

Figure 18. Plot of ζ versus z

Table IX. Measured Lengths of Polymethylene α,ω-Disulfonates

$Na_2(SO_3)_2(CH_2)_n$	X 10^{-8} cm.		
n	a'_{meas}	$2b'$ (center of SO_3 group)	$2b'$ (end of molecule)
2	2.5	5.0	7.3
3	2.5	6.5	8.5
4	2.5	7.5	10.0
5	2.5	9.0	11.4
6	2.5	10.5	12.8
10	2.5	16.5	19.8

Table X. Frictional Coefficients for Perrin Rigid Ellipsoid Model

$Na_2(SO_3)_2(CH_2)_n$	X 10^7 (g/sec)	
n	ζ_{exp}	ζ_{theory}
2	.0497	-----
3	.0524	1.1280
4	.0539	.0642
5	.0549	.0550
6	.0562	.0434
10	.0563	.0355

Figure 19, shows that there is no correlation of data and theory. This theory finds its application in rigid systems of bolaform electrolytes as has been suggested previously.

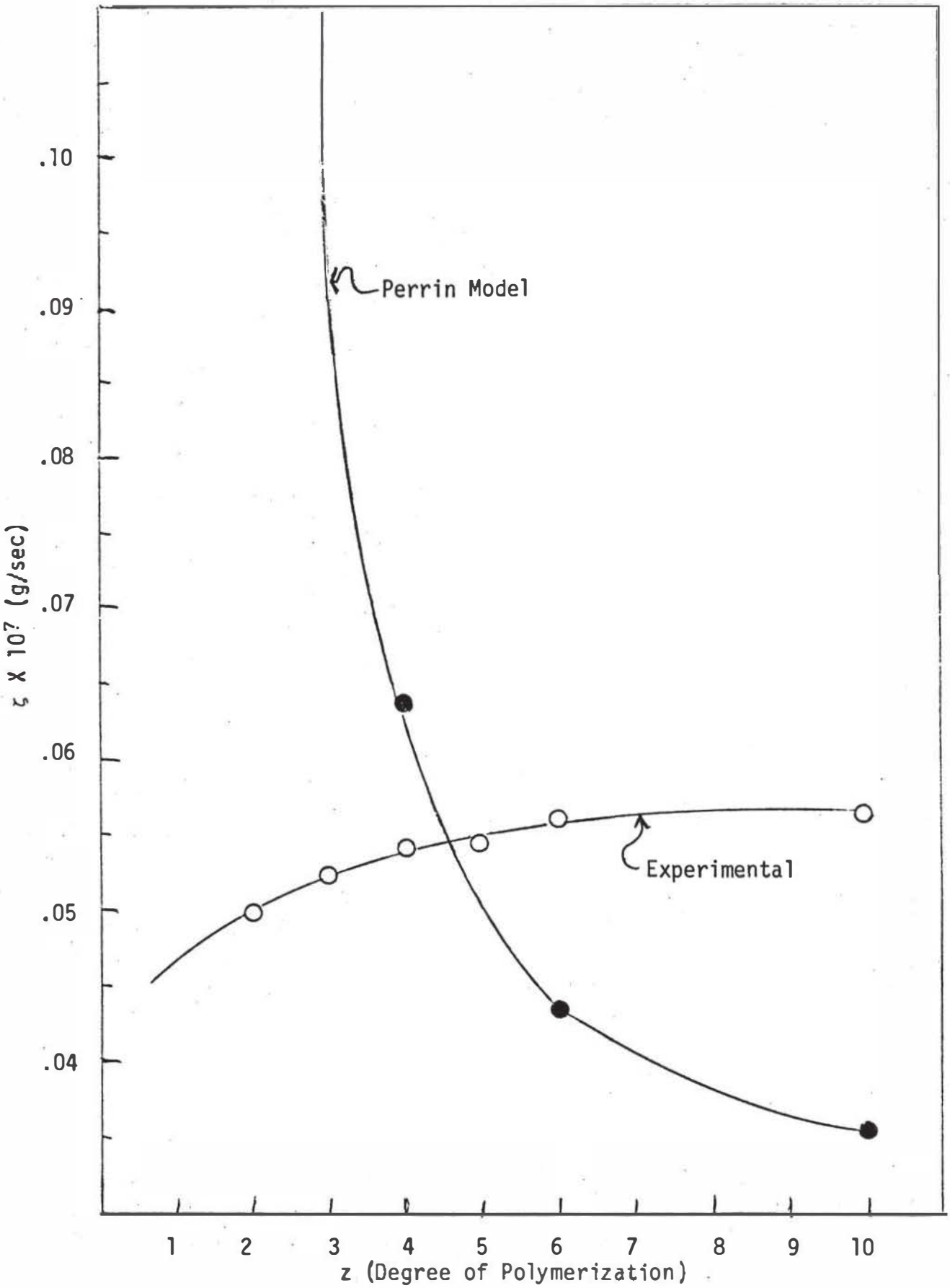

Figure 19. Plot of ζ versus z, Perrin Rigid Ellipsoid Model.

SUMMARY

1. Determination of Frictional Coefficients. The values of the frictional coefficients calculated from experimental parameters and those calculated from the Peterlin rod and bead model agree exceptionally well. It is possible to predict accurate values for molecules of this type utilizing this model. The rigid ellipsoid model of Perrin showed no correlation to experimentally determined frictional coefficients.

2. Unsymmetrical Data Treatment. The sodium α,ω-polymethylene disulfonate salts under investigation, were found to be nearly unassociated in methanol. The equation of Murphy and Cohen did not adequately describe the behavior of these electrolytes in this range of concentration. The Onsager limiting law was used to determine Λ_o values.

3. Symmetrical Data Treatment. The magnesium α,ω-polymethylene disulfonates were found to be greatly associated in methanol. The extent of association could not be calculated utilizing the Murphy-Cohen or Fuoss-Onsager equations. Therefore, Λ_o values were calculated utilizing known λ^+ and λ^- values. The value of K_A for each species was determined utilizing simple graphical techniques. It was found that as the chain length increased the association constant became smaller. This trend is due to the charge density on the molecule decreasing as the charge separation increases.

Proposal of Future Investigations

A continuing program of research of the behavior of non-rigid bolaform electrolytes in solution may be proposed on the basis of this

thesis.

1. The conductance of the salts which are prepared in this thesis should be determined in water. This would allow the properties of the salts, especially the magnesium, to be determined without any interference from ion association.

2. Conductance data could be determined for these salts in solvents which allow one to vary the dielectric constant such as dioxane-water mixture or ethylene glycol and glycerol in which viscosity effects vary.

3. The sodium and magnesium salts of the heptane, octane and nonane may be prepared and the behavior in solution determined in a similar manner to this investigation. It would also be very instructive to increase the chain length to z = 15 or higher. This would indicate whether a "limiting" conductance could be reached in which little variance between successive homologs would be noticed. This could lead to a fundamental knowledge and possibly enable one to predict properties of more complex polyelectrolytes, both synthetic and those occuring in living organisms.

APPENDIX 1

THE MURPHY-COHEN EQUATION FOR UNSYMMETRICAL, N-M, ELECTROLYTES

The equation is:

$$\Lambda = \Lambda^\circ - S\sqrt{C} + E'C\ln C + J'C$$

where $S = \alpha\Lambda^\circ + \beta$:

$$\alpha = \frac{q^2 \kappa/\sqrt{C}\ ab}{3(1+q)} = \frac{2.8012 \times 10^6\ |Z_1 Z_2|\ \omega^{1/2} q^2}{(1+q)(DT^{3/2})}$$

$$\beta = \frac{F\varepsilon\ \kappa/\sqrt{C}\ (|Z_1| + |Z_2|)}{1{,}798{,}755\pi\eta}$$

$$\beta = \frac{41234(|Z_1| + |Z_2|)\omega^{1/2}}{\eta(DT)^{1/2}}$$

$$q^2 = \frac{|Z_1|\,|Z_2|}{(|Z_1|+|Z_2|)} \times \frac{(\lambda_1^\circ + \lambda_2^\circ)}{(|Z_1|\lambda_1^\circ + |Z_2|\lambda_2^\circ)}$$

$$ab = \frac{|Z_1|\,|Z_2|\varepsilon^2}{DkT} = \frac{16.7098 \times 10^{-4}\,|Z_1 Z_2|}{(DT)}$$

$$\kappa/\sqrt{C} = \frac{0.502915 \times 10^{10}\sqrt{\omega}}{(DT)^{1/2}}$$

$$\omega = (\nu_1 Z_1^2 + \nu_2 Z_2^2)$$

$$E' = E_1'\Lambda^\circ - 4E_2'\left[q^2 + \frac{(|Z_1| - |Z_2|)^2}{|Z_1 Z_2|}\right]$$

$$E_1' = \frac{(q\kappa ab)^2}{12C}$$

$$E_2' = \frac{\kappa ab\beta}{16\sqrt{C}}$$

$$J' = \sigma_1'\Lambda^\circ + \sigma_2'$$

$$\sigma_1' = 2E_i'\left[\ln\frac{\kappa ab}{\sqrt{C}} + f(q) + I_1(b)\right]$$

$$f_1(q) = 1.1544314 - \frac{6q + 15q^2 + 21q^3 - 13q^4 - 35q^5 + 6q^6}{12q^2(1+q)(1-q^2)}$$

$$+ \frac{2-q^2(1-q^2)}{2(1-q^2)}\ln(2+q) + \frac{1-2q^2}{1-q^2}\ln(1+2q) + \frac{(1-q^2)^2}{2q^2}\ln(1+q)$$

$$- \frac{(|Z_1| - |Z_2|)^2}{2|Z_1Z_2|(1-q^2)}\left[\frac{1}{3} - \frac{2q^2}{1-q^2}\ln\frac{3}{2+q}\right]$$

$$I_1(b) = \left[\left[e^b(23b^2 + 9b + 12) - 6b^3 - 8b^2 - 9b - 12\right]/18b^3 - E_i(b)\right]$$

$$\sigma_2' = 16E'\left[-\tfrac{1}{2}\left[\frac{(|Z_1| - |Z_2|)^2}{|Z_1Z_2|} + q^2\right]\ln\frac{\kappa ab}{\sqrt{C}} + q^2[f_2(q) + I_2(b)]\right]$$

$$f_2(q) = \frac{18q + 61q^2 + 21q^3 - 6q^4}{48q^2(1+q)} + \left[(45q + 4q^2 - 2q^3 - q^4)\ln(1+q)\right.$$

$$-4(1+q^2)(1-q)\ln(1-q) - (8 + 4q + 8q^2 + 8q^3 + q^4)\ln(2+q)$$

$$\left.+4(1+q^2)(2-q)\ln(2-q)\right]/8q^3 - 0.5772157\Big]$$

$$I_2(b) = \left[\frac{1}{q^2b} + \tfrac{1}{2}E_i(b) + \left[e^b(-5b^2 - 36b^4 + 30b^3 + 30b^2 - 18b - 36 + 6b^4\right.\right.$$

$$\left.+ 45b^3 + 6b^2 + 54b + 36\right]/108b^5 + \frac{1}{q^2|Z_1Z_2|}\xi_s^*(b)$$

$$- \frac{(|Z_1| - |Z_2|)}{2q^2|Z_1Z_2|}(0.5772157 + \ln 3 + 0.16666667 - \ln b)$$

$$- \frac{q^2E_2'}{9E_1'\Lambda^\circ b^4}\left[e^b(b^4 + 5b^3 + 3b^2 - 12b + 6) - \frac{9b^4}{2} - 3b^3 + 6b^2 + \right.$$

$$\left.\left.6b - 6\right]\right]$$

$$\xi_s^*(b) = \sum_{n=3}^{\infty}\frac{(-b/|Z_1Z_2|)^{n-2}}{n!(n-2)}\left[|Z_1|\frac{n}{|Z_1|} - \frac{(-|Z_2|)^n}{|Z_2|}\right]$$

$$E_i(b) = 0.5772157 + \ln b + \sum_{n=1}^{\infty}\frac{b^n}{n!n}$$

APPENDIX 2

COMPUTER PROGRAM [FORTRAN IV]

MURPHY-COHEN EQUATION DATA

TREATMENT

APPENDIX 2

THE MURPHY-COHEN EQUATION FOR UNSYMMETRICAL ELECTROLYTES

```
      DIMENSION (3C),Q(30),QP(30),PQ(30),DELQ(30),AM(20),ABCAP(30)
   10 READ(5,100) N,(AN(I),I=1,19)
  100 FORMAT(I2,19A4)
      AN=N
      IF(N) 1000,1000,105
  105 READ(5,110) D,ETA,T
  110 FORMAT(F6.2,F6.6,F6.2)
      DT=D*T
      READ(5,115)Z1,Z2,QZ,QZ1
  115 FORMAT(2F1.0,2F6.3)
      READ(5,120)(C(I),I=1,N)
  120 FORMAT(12F6.4)
           DO 125 I=1,N
           C(I)=C(I)*1.E-4
      READ(5,130)(Q(I),I=N)
  130 FORMAT(12F6.3)
      IF(Z1-Z2) 135, 140, 135
  135 GNU1=Z2
      GNU2=Z1
      GO TO 200
  140 GNU1=1.
      GNU2=1.
  200 WW=SQRT(0.5*(GNU1*Z1*Z1+GNU2*Z2*Z2))
      CAP=0.502915E10*WW/SQRT(DT)
```

```
      PHI=16.7098E-4*Z1*Z2/DT
      A11=AN
      DO 210 J=1,20
      QS=SQRT(Z1*Z2*QZ/((Z1+Z2)*(Z2*QZ1+Z1*(QZ-QZ1))))
      ALPHA = 2.8012E6*Z1*Z2*WW*QS*QS/((1.+QS)*(DT**1.5))
      BETA =41.243*(Z1+Z2)*WW/(ETA*SQRT(DT))
      EP1=(QS*CAP*PHI)**2/12.
      EP2=CAP*PHI*BETA/16.
      S=ALPHA*QZ+BETA
      EP=EP1*QZ-4.*EP2*(QS*QS+(Z1-Z2)**2/(Z1*Z2))
      PPQZ=QZ
      A12=0.0
      A13=0.0
      A22=0.0
      A23=0.0
      DO205 I=1,N
      QP(I)=Q(I)+S*SQRT(C(I))-EP*C(I)*ALOG(C(I))
      A12=A12+C(I)
      A13=A13+QP(I)
      A22=A22+C(I)*C(I)
  205 A23=A23+C(I)*QP(I)
      DETD=AN*A22-A12*A12
      QZ=(A13*A22-A12*A23)/DETD
      AJ=(AN*A23-A12*A13)/DETD
      IF(ABS(QZ-PPQZ)-0.001) 215, 210,210
  210 CONTINUE
  215 SUMDIF=0.0
```

```
      DO 235 I=1,N
      PQ(I)=QZ-S*SQRT(C(I))+EP*C(I)*ALOG(C(I))+AJ*C(I)
      DELQ(I)=Q(I)-PQ(I)
  235 SUMDIF=SUMDIF+(PQ(I)-Q(I))**2
      SDQ=SQRT(SUMDIF(AN-2.0))
      SDPAJ=SDQ*SQRT(AN/DETD)
      SDPQZ=SDQ*SQRT(A22/DETD)
      WRITE (6,900)
  900 FORMAT(1H1,'PROGRAM2--A LEAST-SQUARES FIT OF UNASSOCIATED UNSY
     1MMETRIC ELECTROLYTES,/,13X,SOLUTION DATA TO A MODIFIED FUOSS-O
     2NSAGER EQUATION,/13X,"YOU GOTTA BE KIDDING")
      WRITE(6,905) (AN(I),I=1,19)
  905 FORMAT (1H0,19A4)
      WRITE (6,910)D,ETA,J
  910 FORMAT('SOLVENT DATA'7X'--'8X' D='5X,F7.3,8X'ETA '6X,F9.6,6X'T=

     1'5X,F6.2)
      QZ2=QZ-QZ1
      WRITE(6,915)Z1,Z2,QZ1,QZ2
  915 FORMAT('SOLUTE DATA'8X'--'7X' Z1='7X,F2.0,12X'Z2='7X,F2.0,10X,
     1QZ1='5X,F7.3,4X,'QZ2='5X,F7.3)
      WRITE(6,925)N
  925 FORMAT('MISCELLANEOUS'6X'--'8X'N=6X,I2)
      WRITE(6,930) QZ,SDPQZ
  930 FORMAT91X/'0  QZ='4X,F8.3,5X'SDPQZ='4X,F8.3)
      WRITE(6,935)S,ALPHA, BETA
  935 FORMAT('6X'S='4X,F7.2,6X,'ALPHA='6X,F8.5,5X,'BETA='4X,F8.4)
```

```
      WRITE(6,940)EP,EP1,EP2
  940 FORMAT(5X'EP= 'F9.2,8X'EP1='5X,F9.5,6X,'EP2='3X,F9.4)
      WRITE(6,945)AJ,SDPAJ
  945 FORMAT(4X'AJ= 'F9.2,6X'SDPAJ='F9.2)
      WRITE(6,960)SDP,J
  960 FORMAT(4X'SDQ='5X,F7.3,9X,'J= '4X,I2)
      WRITE(6,965)
  965 FORMAT(1X/1X/1X'    'I    C(I)      Q(I)      PQ(I)      DELQ(I)
     1QP(I) KAPPA*A*B(I)'/1X)
           DO 990 I=1,N
      ABCAP(I)=PHI*CAP*SQRT(C(I))
      C(I)=C(I)*1.E4
      WRITE(6,970)I,C(I),Q(I),PQ(I),DELQ(I),QP(I),ABCAP(I)
  990 CONTINUE
  970 FORMAT(1X,I2,3X,F8.4,3X,F7.3,3X,F7.3 ,3X,F7.3,3X,F7.3,9X,F7.5)
      GO TO 10
 1000 CONTINUE
      RETURN
      END
$ENTRY
```

LIST OF REFERENCES

1. G. Atkinson and S. Petrucci, J. Chem. Phys. 67, 333 [1963].
2. B. Staples and G. Atkinson, J. Phys. Chem. 71, 667 [1967].
3. L. Onsager, Physik Z. 28, 277 [1927].
4. L. Onsager and R. M. Fuoss, J. Phys. Chem. 36, 2689 [1932].
5. R. M. Fuoss and D. Edelson, J. Am. Chem. Soc. 85, 2537 [1963].
6. Staples, B. R., The Conductance of Some Rigid Bolaform Electrolytes, Unpublished Masters Thesis. University of Maryland, p. 29 [1965].
7. T. J. Murphy and E. G. D. Cohen, J. Chem. Phys. 53, 6 [1970].
8. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworth Scientific Publications, London, p. 119 [1959].
9. S. A. Rice, J. Am. Chem. Soc. 80, 3207 [2958].
10. S. A. Rice and M. Nagasawa, Polyelectrolyte Solutions, vol. 2, Academic Press, New York. Ch. 6 [1961].
11. A. Peterlin, J. Chim. Phys. 47,7-8, 669 [1950].
12. A. Peterlin, ibid., 48, 1-2, 13 [1951].
13. A. Peterlin, J. Polymer Sci. Vol. 8, 2, 173 [1951].
14. J. Riseman and J. G. Kirkwood, J. Chem Phys. 18, 512 [1950].
15. F. Perrin, J. Phys. Rad. 7, 1 [1936].
16. G. Atkinson and S. Petrucci, J. Phys. Chem. 67, 1880 [1963].
17. B. R. Staples and G. Atkinson, ibid., 73, 3, 520 [1969].
18. G. Thompson, S. A. Rice and M. Nagasawa, J. Am. Chem Soc. 85, 2537 [1963].
19. R. M. Fuoss and V. H. Chu, J. Am. Chem. Soc. 73, 949 [1951].
20. O. N. Brody and R. M. Fuoss, J. Phys. Chem. 60, 156 [1956].
21. S. M. McElvain, A. Jelinek and K. Rorig,J. Am. Chem. Soc. ibid., 67, 1578 [1945].

22. G. C. H. Stone, ibid., 58, 488 [1936].

23. S. Zuffanti and R. Hendrickson, ibid., 63, 2999 [1941].

24. O. V. Brody and R. M. Fuoss, ibid., 60, 157 [1956].

25. R. M. Fuoss and F. Accascina, Electrolytic Conductance, Interscience Publishers, Inc., N. Y. [1959].

26. J. P. Butler, J. I. Schiff and A. R. Gordon, J. Chem. Phys 19, 6 [1951].

27. J. Cauper and M. de Maine, Proc. Roy.Soc., [London], A 127, 228 [1928].

28. H. S. Harned and B. B. Owens, The Physical Chemistry of Electrolyte Solution, 3rd ed., Reinhold Publishing Corp., New York, [1958], pp.232 and 697.